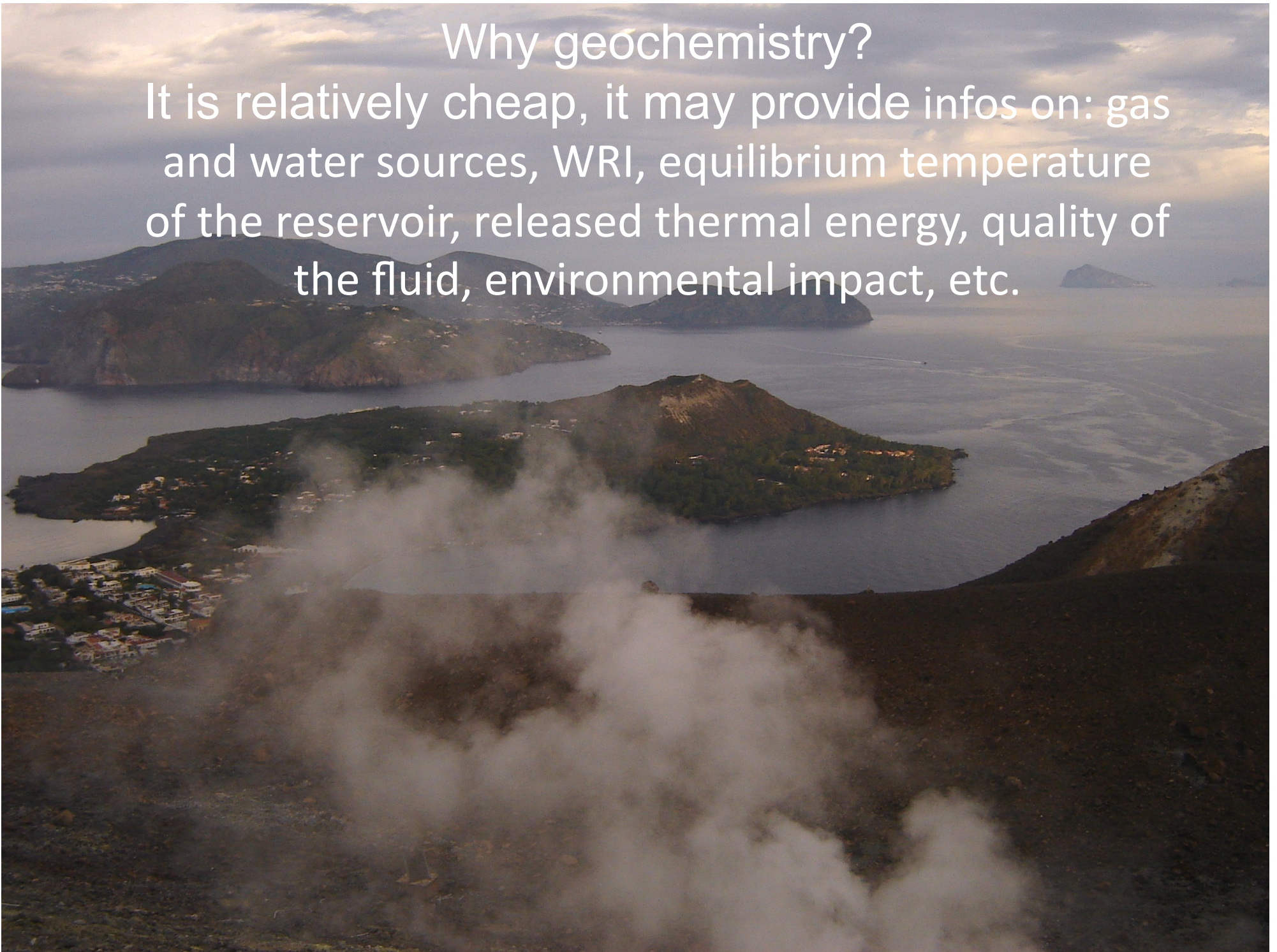
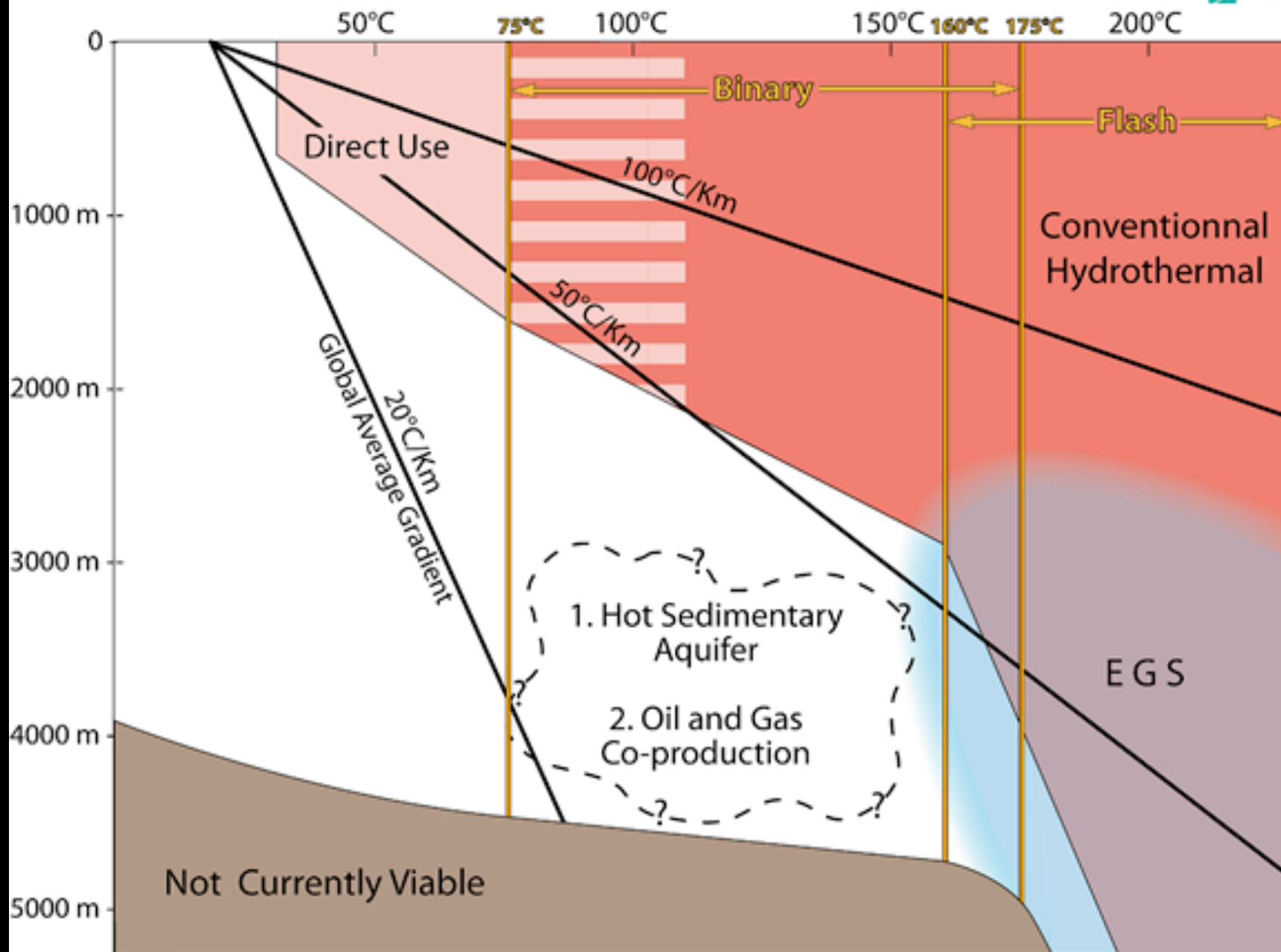


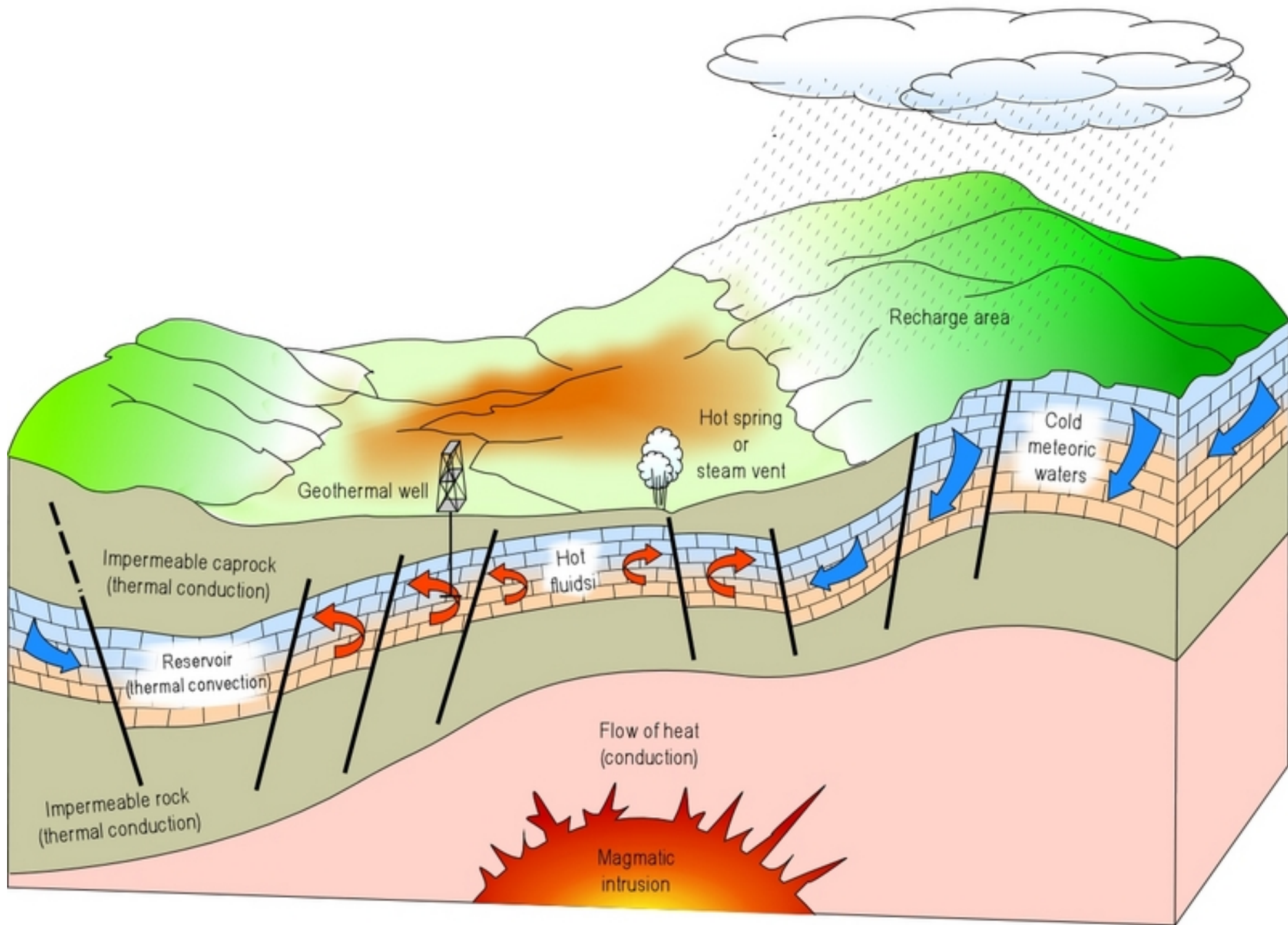
Why geochemistry?

It is relatively cheap, it may provide infos on: gas and water sources, WRI, equilibrium temperature of the reservoir, released thermal energy, quality of the fluid, environmental impact, etc.



Schematic Depth-Temperature Plot for Geothermal Resources







Interaction between
magmatic...

...and hydrothermal fluids



Generally, higher T°C

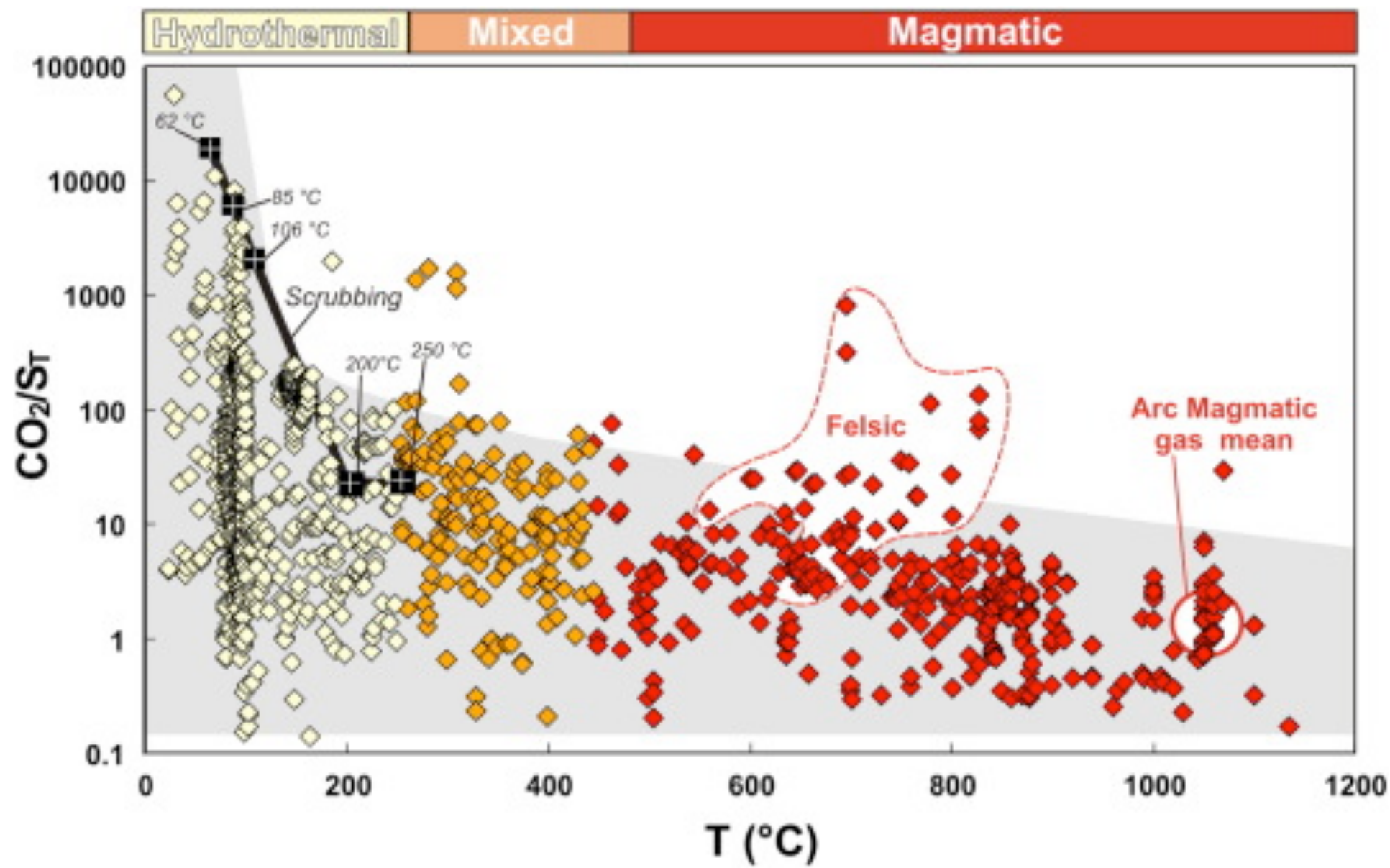
Table 1: Characteristic composition of volcanic gases at the vent (e.g., Symonds et al. 1988, Cadle 1980, Symonds et al. 1994, and Chin and Davis 1993, see also table 2).

Species	H ₂ O	CO ₂	SO ₂	H ₂ S	COS	CS ₂	HCl	HBr	HF
%/vol	50-90	1-40	1-25	1-10	$\frac{10^{-4}-10^{-2}}$	$10^{-4}-10^{-2}$	1-10	?	< 10 ⁻³
Tg/year	?	75	1.5-50	1-2.8	0.006-0.1	0.007-0.096	0.4-11	0.0078-0.1	0.06-6

Generally, lower T°C

Table 1. Chemical Composition of the Dry Gas Fraction (Inorganic Gases) and Outlet Temperatures of the Fumaroles and the Geothermal Wells From the Ahuachapan-Chipilapa, Berlin-Chinameca, and San Vicente Geothermal Fields^a

	Name	Location	T, °C	CO ₂	H ₂ S	N ₂	Ar	O ₂	Ne	H ₂	He	CO	H ₂ O	CH ₄
1	El Playon	Ahuachapan	99.4	828,965	1,266	157,977	852.8	992.1	0.561	9,988	4.196	1.189	992,930	147.1
2	Chipilapa	Ahuachapan	99.7	948,492	2,954	46,294	92.18	1,463	0.056	698.6	8.170	1.216	996,116	40.67
3	Agua caliente M2	Ahuachapan	99.2	952,606	31,180	15,587	160.8	7.184	0.096	486.4	5.044	<0.001	988,168	86.39
4	Zapote	Ahuachapan	101.7	893,874	4,608	91,500	620.4	6,563	0.406	2,799	18.36	1.117	995,991	51.07
5	Termopilas hervideros	Ahuachapan	94.7	932,148	2,551	59,118	670.3	1,199	0.432	4,324	10.52	1.831	993,760	89.66
6	Termopilas fumarola	Ahuachapan	100.5	943,767	4,610	47,607	367.2	59.31	0.237	3,454	9.324	1.960	995,987	82.10
7	El Tortuguero hervideros	Ahuachapan	93.0	951,050	10,320	35,114	118.4	1,444	0.066	1,912	4.725	1.745	988,377	56.14



Differently from other geological disciplines operating in Geothermics, (Fluid) Geochemistry allows a direct contact with what it is commonly discharged from a geothermal reservoir

Thermal and mineral waters

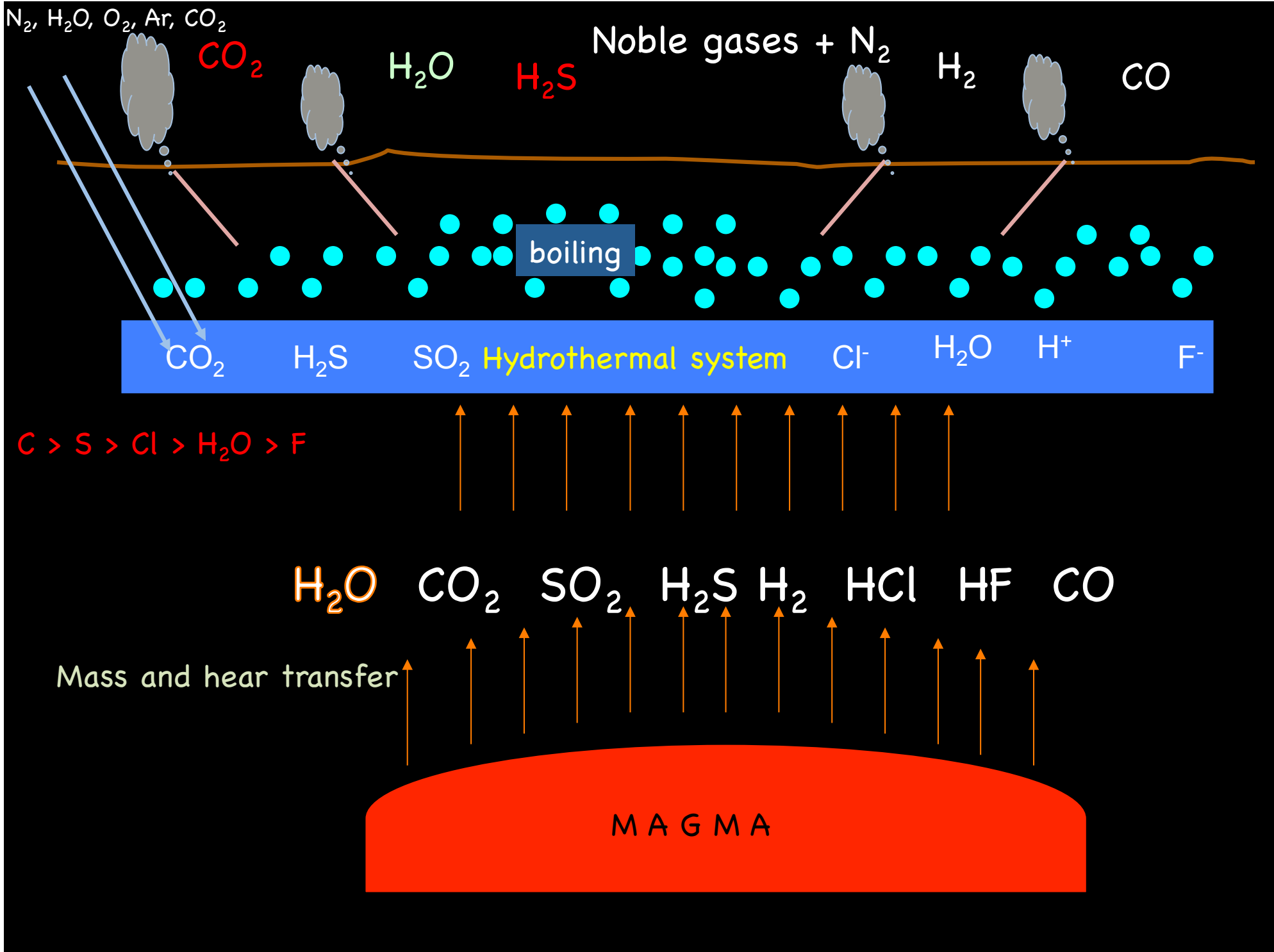


Soil diffuse gas



Gas discharges: bubbling & boiling pools and fumaroles





Secondary interactions

"Magmatic gas scrubbing"

"any process able to reduce emissions during reactions between gas, water and rocks (dissolution, formation of precipitates, gas-water chemical reactions etc.)"

Each single chemical and isotopic composition we obtain is of paramount importance since it reflects a direct information from underground.

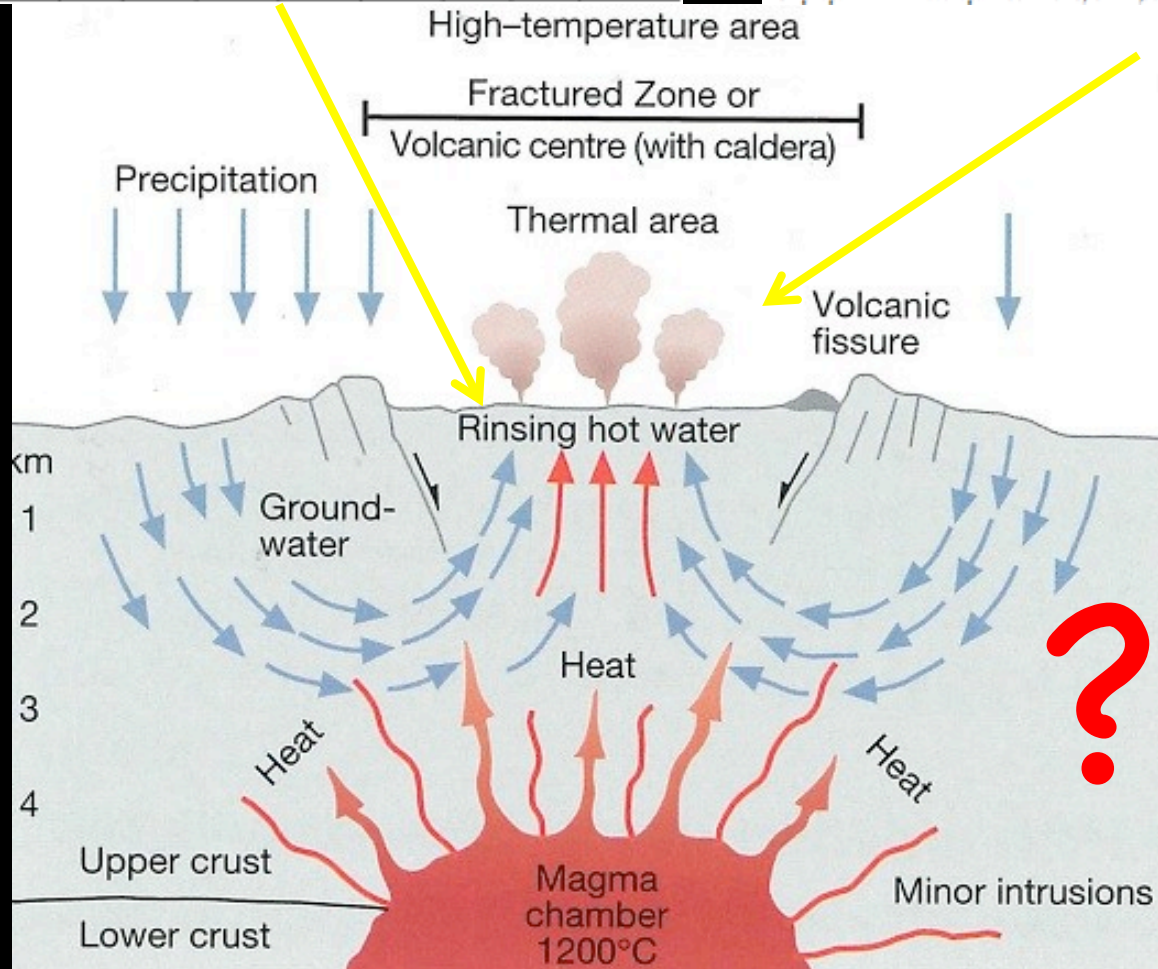
There is a (big) problem

Gas and isotopic composition

Water and isotopic composition

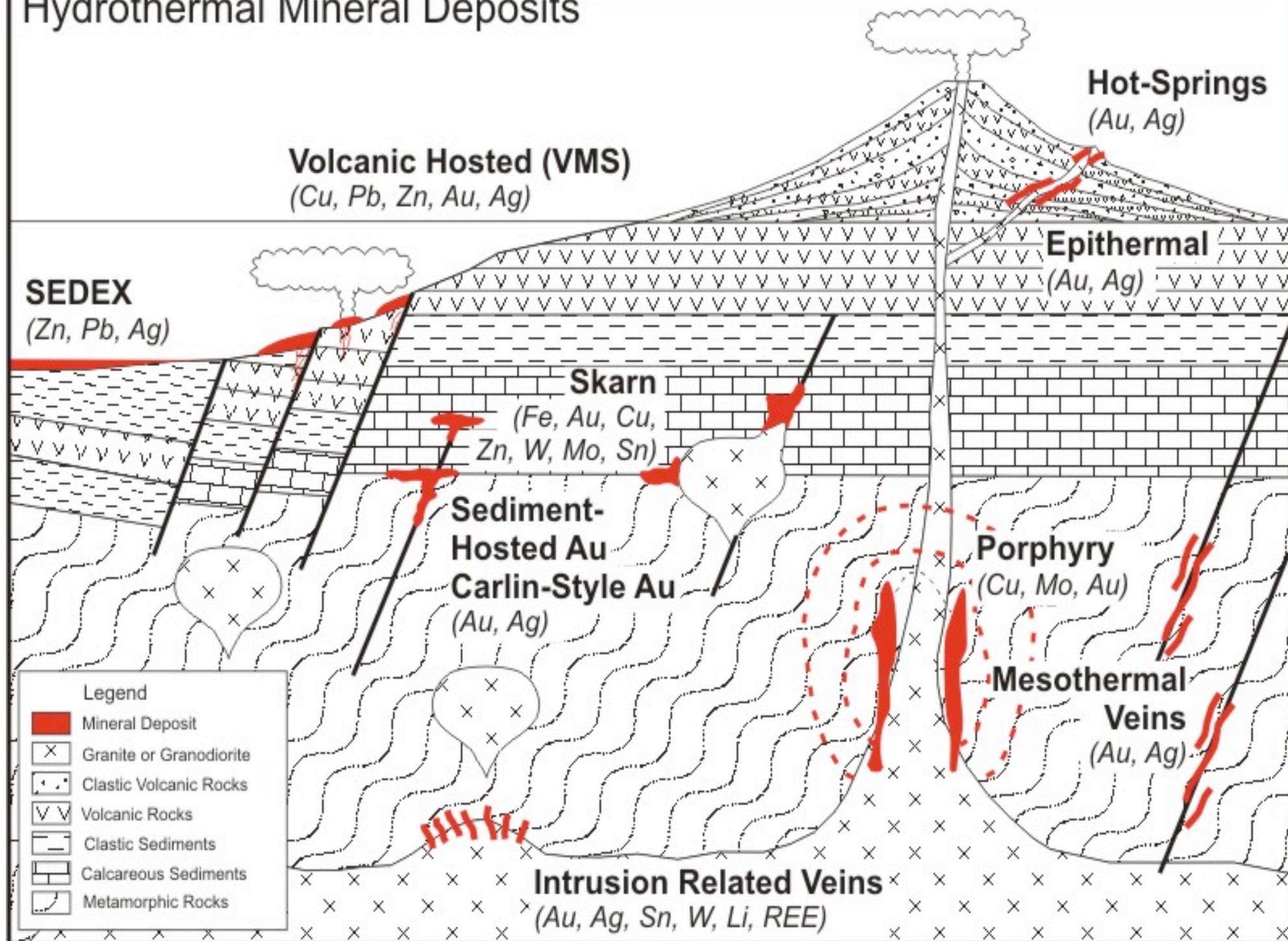
Locality	T°C	pH	HCO ₃	Cl	SO ₄	Na	K	Ca	Mg
Chianciano	39.6	6.09	884	17	1613	20	5.1	620	157.00

Name	Location	T, °C	CO ₂	H ₂ S	N ₂	Ar	O ₂	Ne	H ₂	He	CO	H ₂ O
El Playon	Ahuachapan	99.4	828,965	1,266	157,977	852.8	992.1	0.561	9,988	4.196	1.189	992,930
Chipilapa	Ahuachapan	99.7	948,492	2,954	46,294	92.18	1,463	0.056	698.6	8.170	1.216	996,116



Which is the meaning of the chemical and isotopic compositions we measure at the surface?


Hydrothermal Mineral Deposits



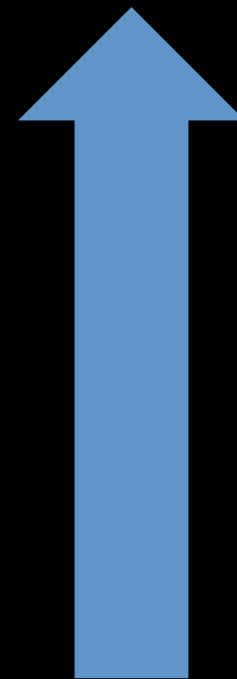
Mineral precipitations at surface

- 1) Calcite (almost always oversaturated)
- 2) Silica (strictly temperature-dependent)
- 3) Fe-hydroxides (strongly pH and Eh dependent)
- 4) Hg-Sb-As-sulphides (in volcanic areas)





Hydrothermal fluid (red),
lower T: scrubbing processes



Magmatic fluid (ox): high T, f
(magma comp., degassing
state, flux, etc.)

Physico-chemical Analyses

Components in the liquid phase: Ca, Mg, Na, K, HCO₃, CO₃, SO₄, Cl, SiO₂, NH₄, NO₃, F, Br, Li, B, S^{II}, CO₂, Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mn, Mo, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, Th, Tl, U, V, W, Zn, Zr

Physical parameters: T, pH, Eh, p_{H₂S}, p_{NH₃}, p_{O₂}, p_{CO₂}

Components in the gas phase: H₂O, CO₂, SO₂, H₂S, N₂, HCl, HF, Ar, NH₃, CH₄+hydrocarbons, O₂, H₂, Rare gases

Dissolved gas: CO₂, N₂, Ar, CH₄, O₂, Ne, H₂, He

Isotopes: ¹⁸O/¹⁶O; D/H; ¹³C/¹²C in DIC (Dissolved

Inorganic Carbon); ¹³C/¹²C in CO₂, ³He/⁴He, ⁸⁷Sr/⁸⁶Sr

Basic concepts

- Geochemical prospecting is economically sustainable and a lot of info can be gathered;
- Waters and gases at the surface **"HAVE BEEN THERE"** and generally they carry "infos" from the depth... it has to be understood WHICH ARE THE INFOS!
- We can divide the fluid constituents into two groups:
 - **Inert (non reactive) constituents** that can be defined as **TRACER!**
Once in solution or in the gas phase they do not change. They are a **TAG** to understand their origin;
 - Chemically reactive species. They are affected by the environment but their behavior is controlled and can be understood: **GEOINDICATORS**

TRACER: Noble gas and N_2 , Cl, B, Li, Rb, Cs

GEOINDICATORS: Na, K, Mg, Ca, SiO_2 (T-dependent when reacting with Al-sils);
 H_2 , H_2S , CH_4 e CO_2 (PT-redox-dependent)

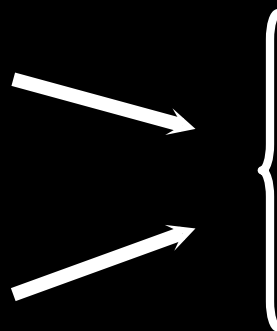
Exceptions: at >250 °C Cesium is a **tracer** but it may be hosted in zeolites at lower temperatures

Geothermometry

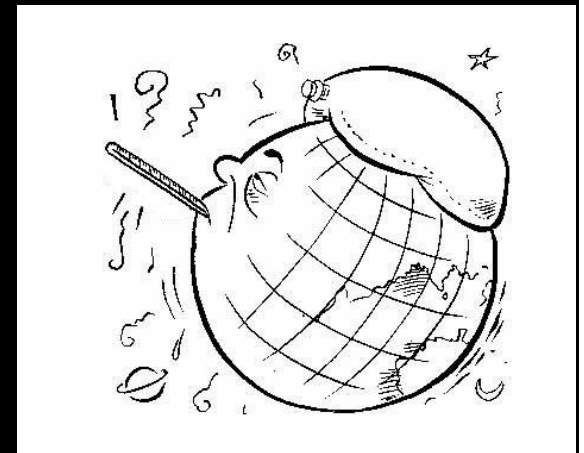
Temperature estimations of the geothermal reservoirs by using mathematical equations that include analytical data

- Chemical GeoT

- Isotopic GeoT



- minerals
- solutions
- gases



Empirical Geothermometers

Comparing concentrations or conc/conc ratios with measured T; good T interval and good T measured at depth

Thermodynamic Geothermometers at chemical/isotopic equilibrium

Calculating the conc/conc ratios for a specific reactions by using the thermodynamic constants related to a specific reaction

Main gases

H₂O

SO₂

H₂S

HF

HCl

CO₂

CO

CH₄ + hydrocarbons

Noble gases (He, Ar, Ne, Kr, Xe, Rn)

H₂

NH₃

N₂

CFC, COS, S₂, heavy metals

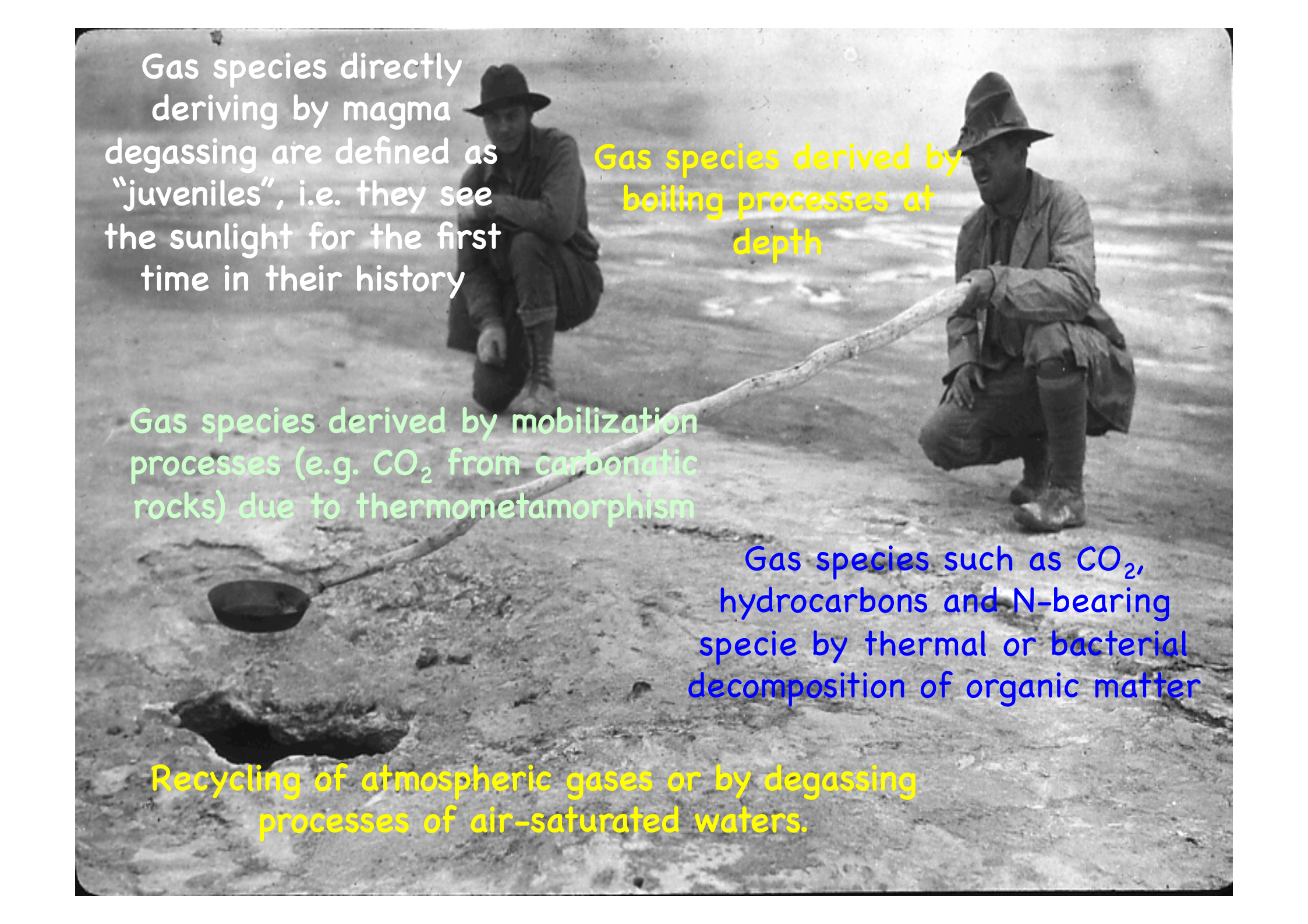
Acidic gases

Isotopes

- Essential: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in H₂O, $^3\text{He}/^4\text{He}$, $\delta^{13}\text{C}$ in CO₂;

- Very Useful: ^3H in H₂O, $\delta^{34}\text{S}$ in S-bearing species,

- Useful: $\delta^{13}\text{C}$ and $\delta^2\text{H}$ in CH₄, $\delta^2\text{H}$ in H₂, $\delta^{15}\text{N}$ in N₂, $^{40}\text{Ar}/^{36}\text{Ar}$, etc.



Gas species directly deriving by magma degassing are defined as "juveniles", i.e. they see the sunlight for the first time in their history

Gas species derived by boiling processes at depth

Gas species derived by mobilization processes (e.g. CO_2 from carbonatic rocks) due to thermometamorphism

Gas species such as CO_2 , hydrocarbons and N-bearing specie by thermal or bacterial decomposition of organic matter

Recycling of atmospheric gases or by degassing processes of air-saturated waters.

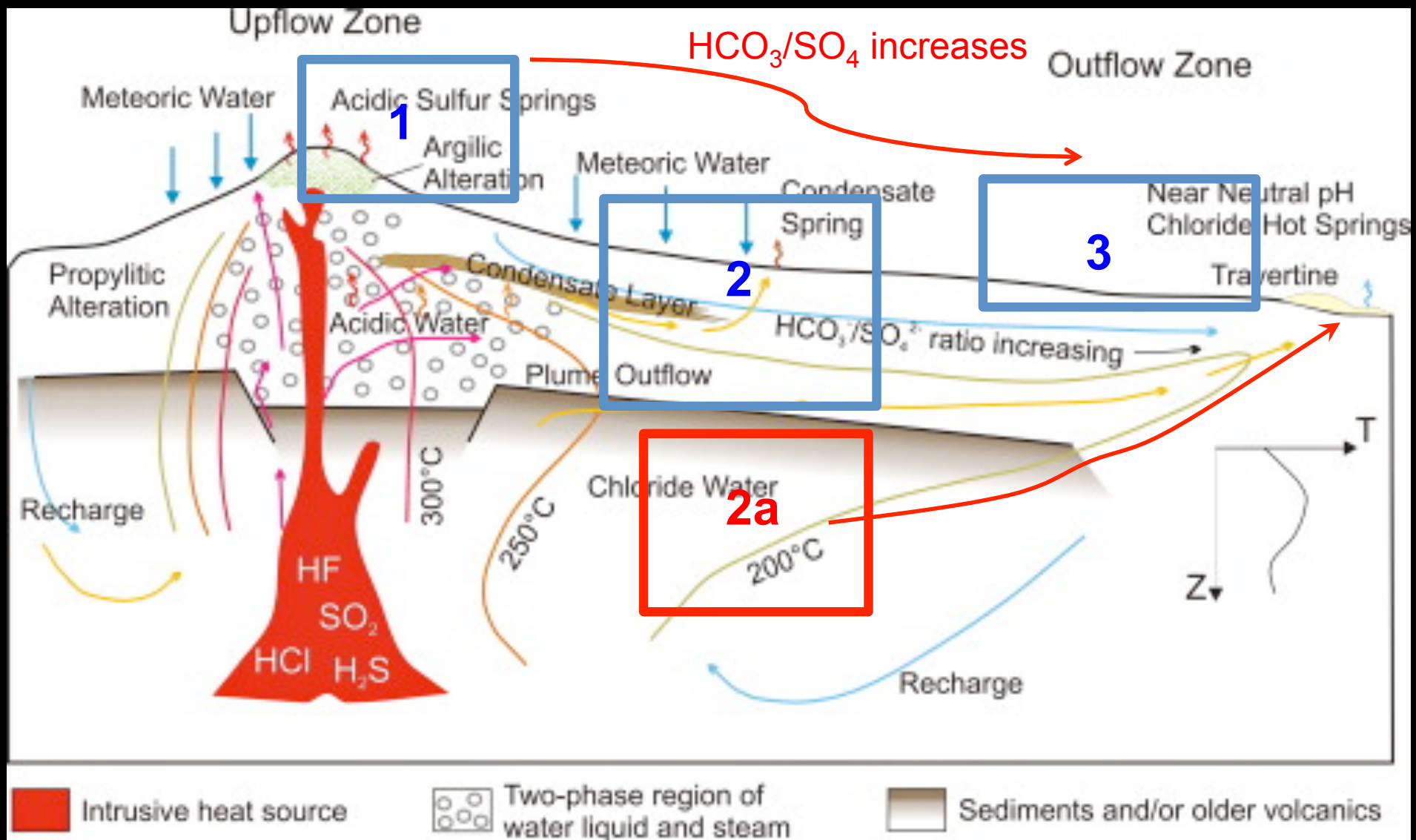
Main water parameters and dissolved components

T °C
pH
Na⁺
K⁺
Mg²⁺
Ca²⁺
HCO₃⁻
CO₃²⁻
Cl⁻
SO₄²⁻
Li⁺
NH₄⁺
F⁻
Br⁻
NO₃⁻
ΣS²⁻
B
SiO₂
Mn²⁺
Fe³⁺
Fe²⁺
Sr²⁺
Ba²⁺
Rb⁺

Water-rock-gas interaction processes + deep-seated input to the surface + salt precipitation/dissolution

Volcanic condensates are normally acidic





Solutes: main anions

Chloride

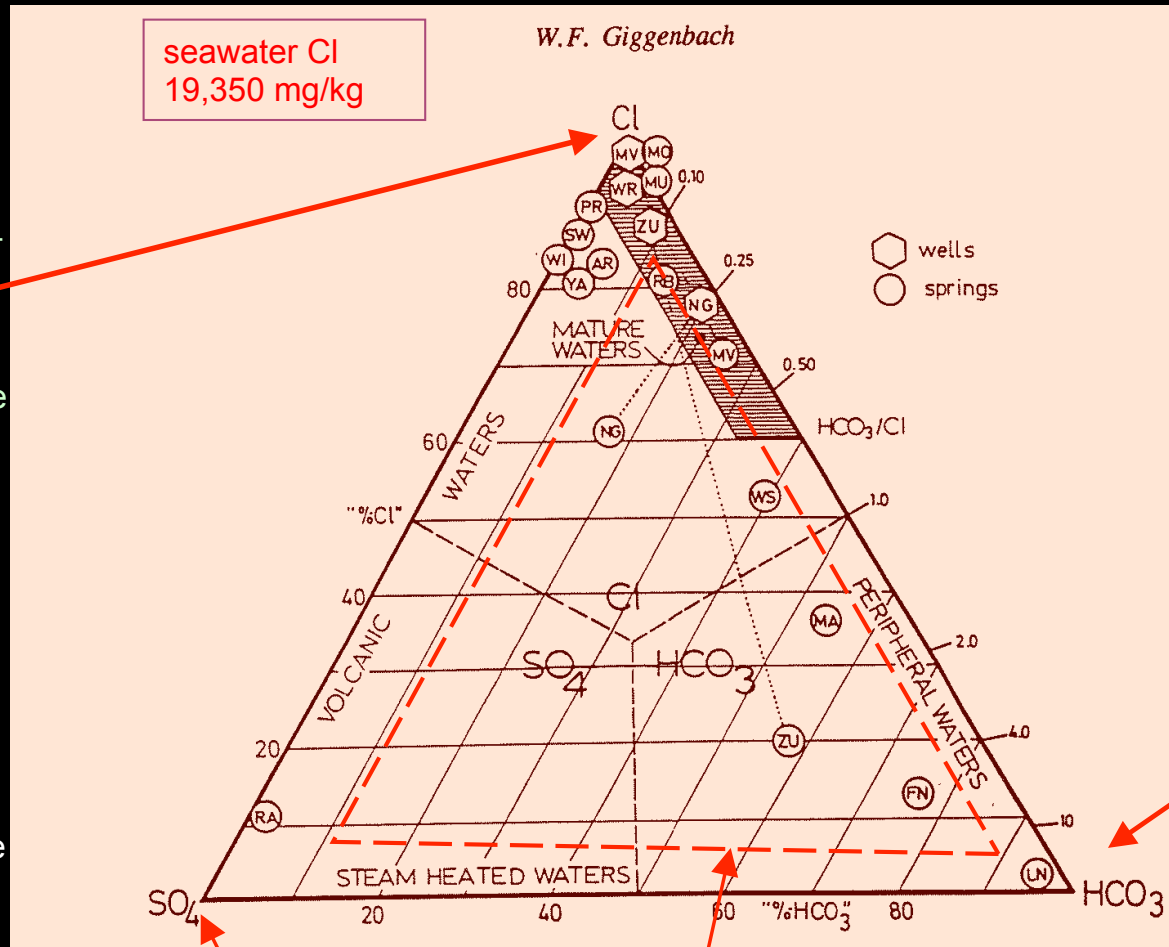
~50 to ~20,000 mg/kg
(to ~200,000 mg/kg in hypersaline brines)

Sources: traces of Na-K-Cl in volcanic rocks (seawater origins), connate seawater in sedimentary rocks, halite deposits

Sulfate

~10 to ~1500 mg/kg
(to ~100,000 mg/kg in acid volcanic steam condensates)

Sources: oxidized sulfide minerals and H₂S, sulfate mineral deposits (gypsum, anhydrite)



Extremes of volcanic and steam heated are acidic (no HCO₃)

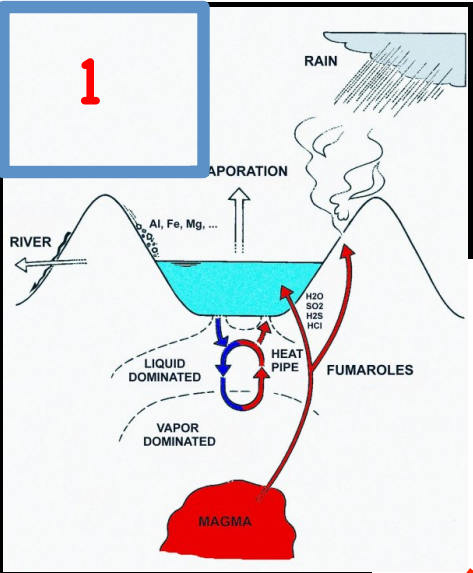
Approximate range among non-volcanic geothermal systems (higher SO₄ exist)

Bicarbonate

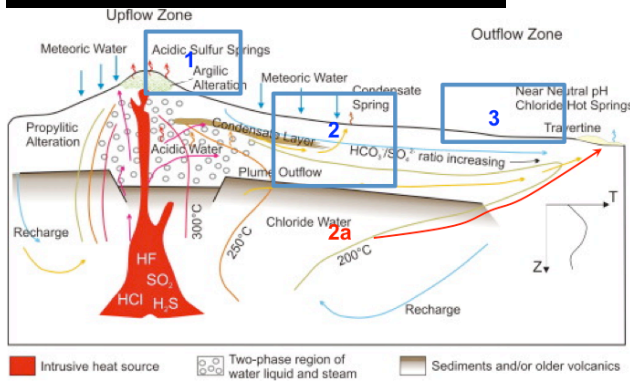
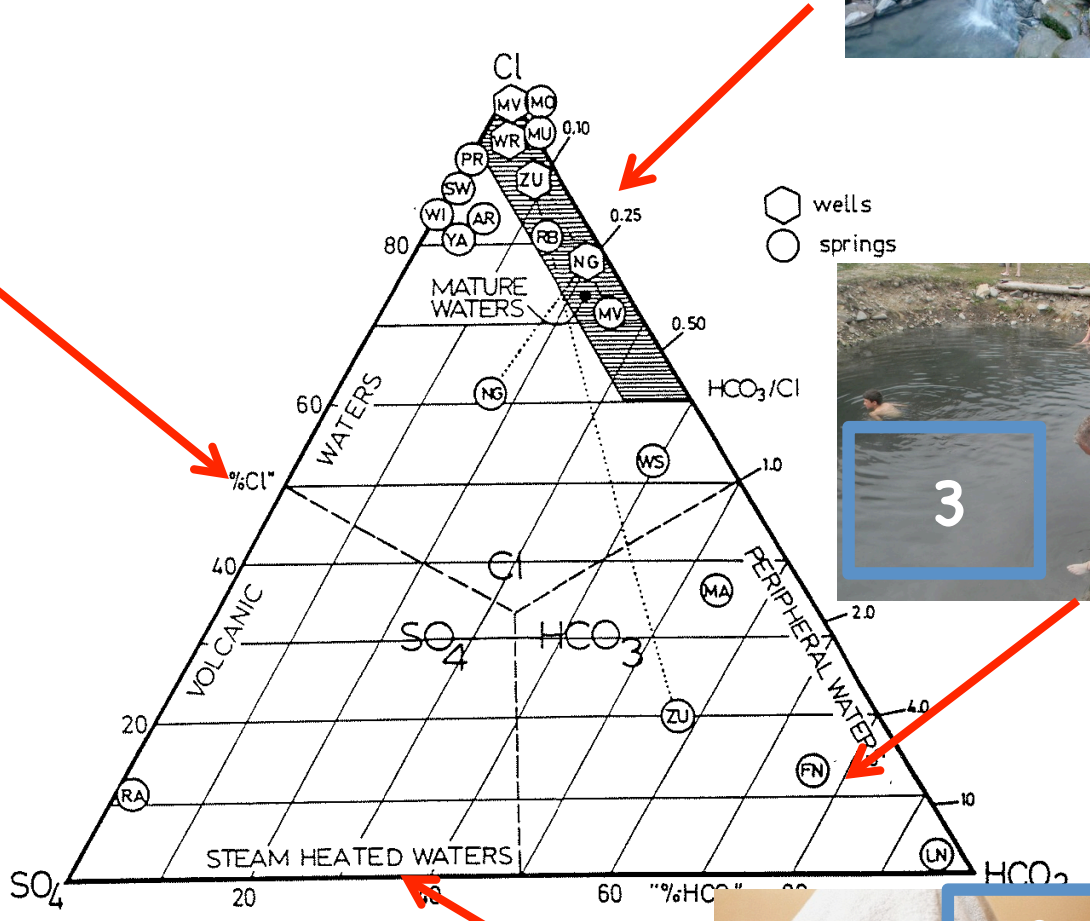
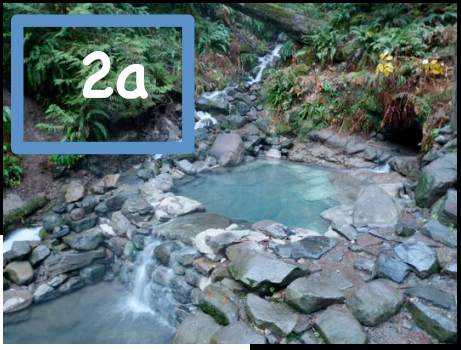
<1 to several 1000 mg/kg

(for most purposes, effectively the same as "alkalinity")

Sources: reactions of dissolved CO₂ from atmosphere and/or in geothermal/volcanic steam, with silicate minerals in rocks, with carbonate minerals (limestone)

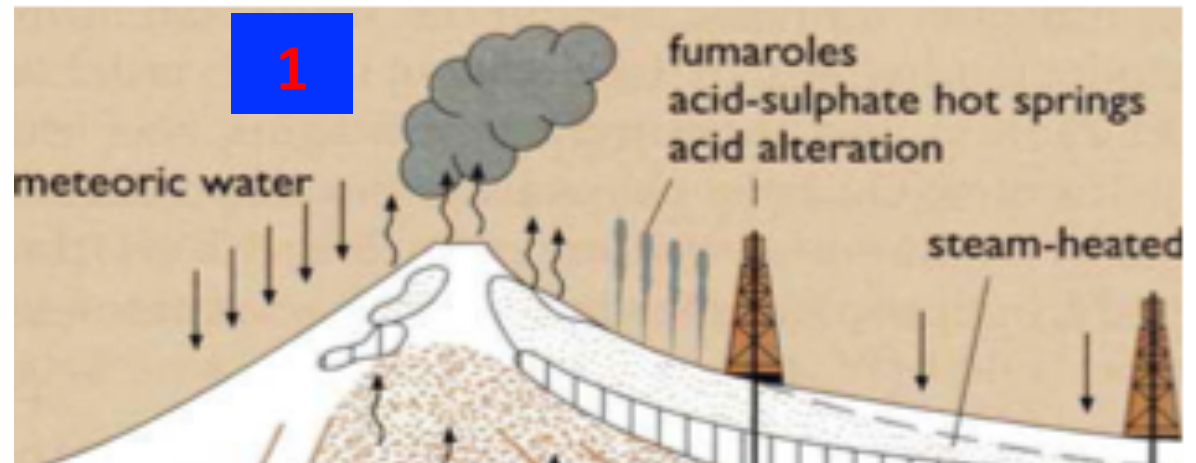


The waters at depth are initially acidic and turn to be neutral Na-Cl waters due to WRI processes and removal of magmatic sulfur species by transformation to sulfate/sulfide.



Acque Cl-SO₄ acide

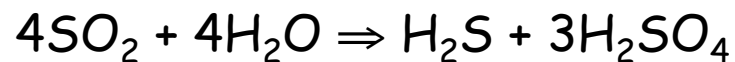
Tipiche di crater lakes come El Chichón, Kawah Ijen, Poás, Sirung, Yugama e Yakeyama.



La chimica di tali sistemi è interessata da inflow di gas magmatici ricchi in HCl, SO₂ e H₂S, con produzione di soluzioni acide fortemente reattive.

Scarsità di H₂O acide a Cl-SO₄ - SO₄-Cl in reservoir geotermici di sistemi vulc.

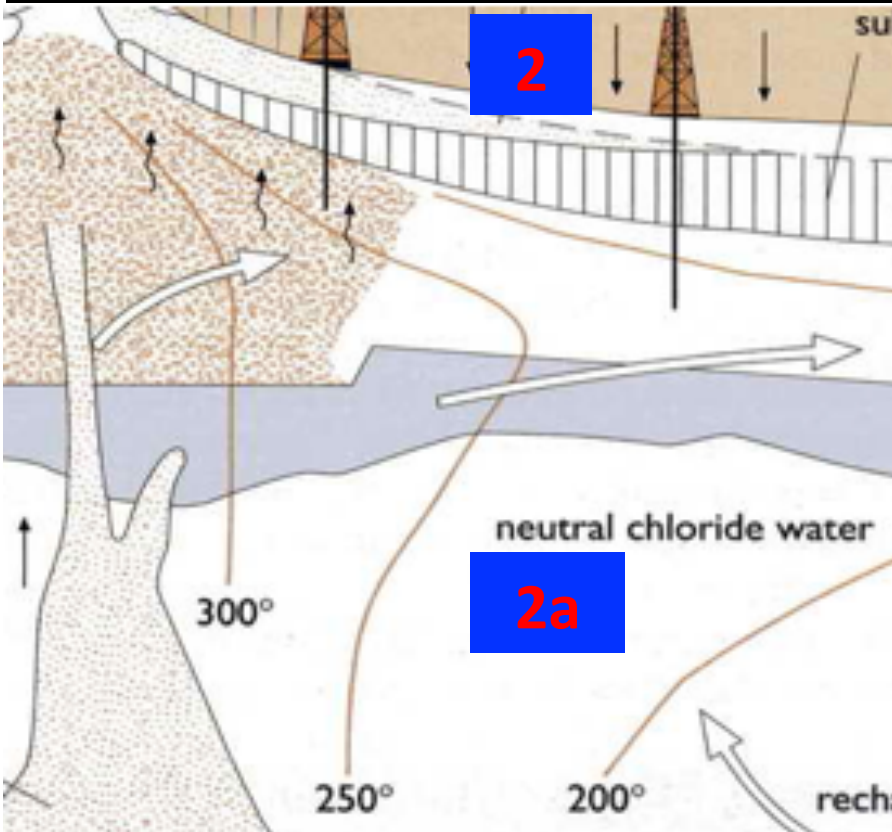
L'SO₂ disproporziona:



Queste soluzioni acide ossidate sono altamente reattive lisciviando cationi dalle rocce ospiti con deposizione di alunite, anidrite, pirite e caolinite.

La bassa disponibilità di rocce nell'ambiente lacustre previene il processo di neutralizzazione. In profondità i gas magmatici interagiscono con quantità di acqua e rocce maggiori di quanto avvenga in superficie. È qui che presumibilmente si formano le acque neutre ricche in NaCl.

Tipi di acque



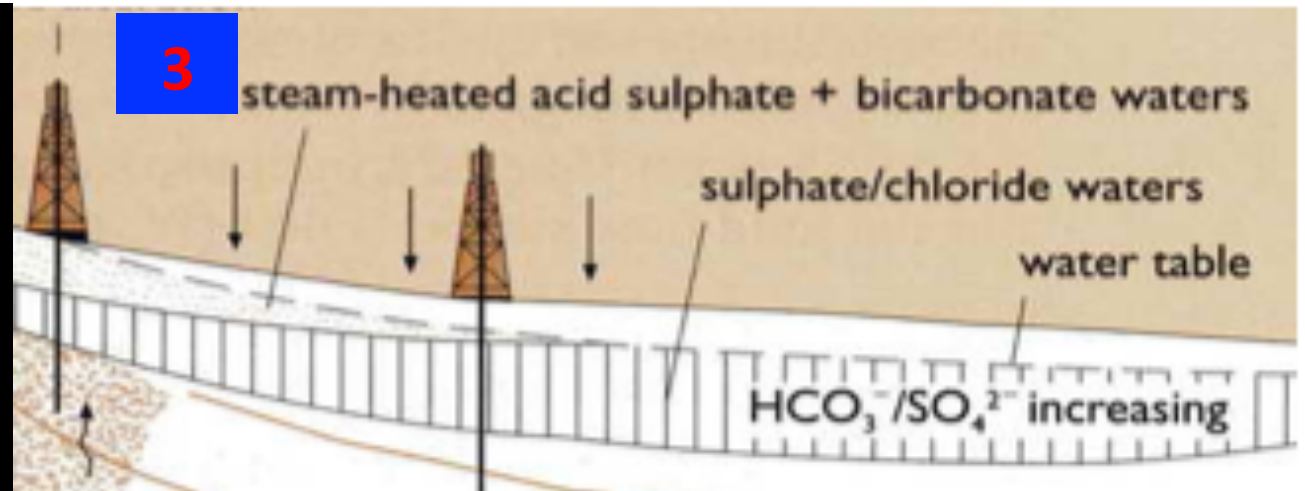
Le acque circolanti in serbatoi geotermici profondi e di alta entalpia: **Na-Cl** con Cl sino a migliaia di mg/L (155.000 mg/L; Salton Sea, California) con pH da acidi a neutri ed alto SiO_2 , K, Li, B e F, basso Mg. I gas disciolti principali sono CO_2 and H_2S . Sono alimentate da acqua meteorica ma possono avere anche imprinting di acque connate o saline di altra natura.

In sistemi associati ad edifici vulcanici si possono avere HCl, HF, SO_2 , e H_2S e CO_2 con $\text{H}_2\text{O}_{\text{andesitica}}$. La conversione di soluzioni inizialmente acide a Na-Cl neutre richiede reazioni WR e rimozione delle specie sulfuree magmatiche per trasformazione a solfati/solfuri.

Le acque profonde Na-Cl possono giungere sino alla superficie ed essere rilasciate da boiling pool con pH da neutri ad alcalini. O mescolarsi con acque più superficiali producendo soluzioni acquose con Cl diluito. Molto spesso, tali acque possono ritrovarsi a vari km di distanza dall'edificio vulcanico in questione.

Acque solfato acide
riscaldante da vapore

Si trovano generalmente
sopra il sistema
geotermico dove avviene
la separazione di vapore.



L'ebollizione comporta il transfer delle specie gassose quali CO₂ e H₂S nella fase vapore. Tale vapore può reagire con acquiferi/acque superficiali.

Alternativamente il vapore può condensare (parzialmente) in tali sistemi producendo "STEAM-HEATED WATERS". Qui H₂S si ossida ad acido solforico producendo acque solfato acide. Bassi sono i valori di Cl e pH (0-3) che reagiscono velocemente con la roccia ospite per produrre alterazioni argillitiche (caolinite ed alunite).

I cationi disciolti sono da lisciviazione di rocce ospiti.

Le STEAM-HEATED WATERS possono andare in ebollizione, separando un vapore secondario che raggiunge la superficie come low-pressure steaming grounds.

Acque bicarbonato-sodiche

Si originano per dissoluzione di gas contenenti CO_2 o per condensazione di vapore geotermico in acquiferi relativamente profondi in sistemi privi di O_2 che prevengono l'ossidazione H_2S e l'acidità è conferita dalla dissociazione di H_2CO_3 .

Sebbene sia un acido debole questo converte i feldspati a minerali argillosi con produzione di soluzioni neutre $Na-HCO_3$, poiché:

- i) La bassa solubilità della calcite previene l'arricchimento in Ca;
- ii) K e Mg sono nei minerali argillosi e cloriti;
- iii) La concentrazione di SO_4 è limitata dalla solubilità dell'anidrite.

Tali acque si trovano generalmente nelle zone di condensazione di sistemi dominati da vapore e nelle parti marginali dei sistemi dominati da acqua. Possono tuttavia essere presenti in reservoir profondi situati all'interno di rocce metamorfiche e/o sedimentarie (e.g. Kizildere, Turkey).

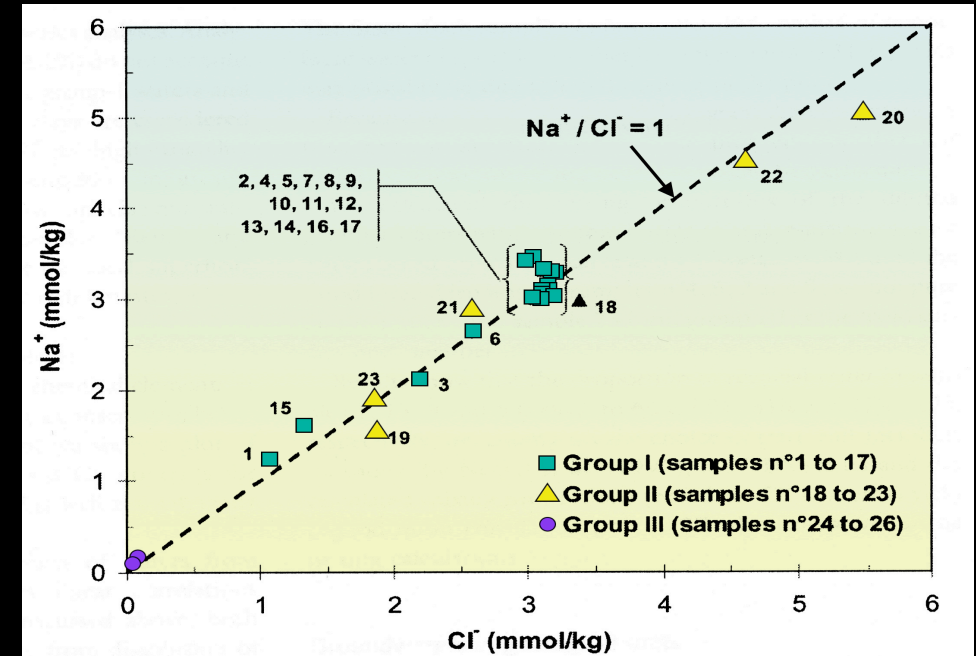
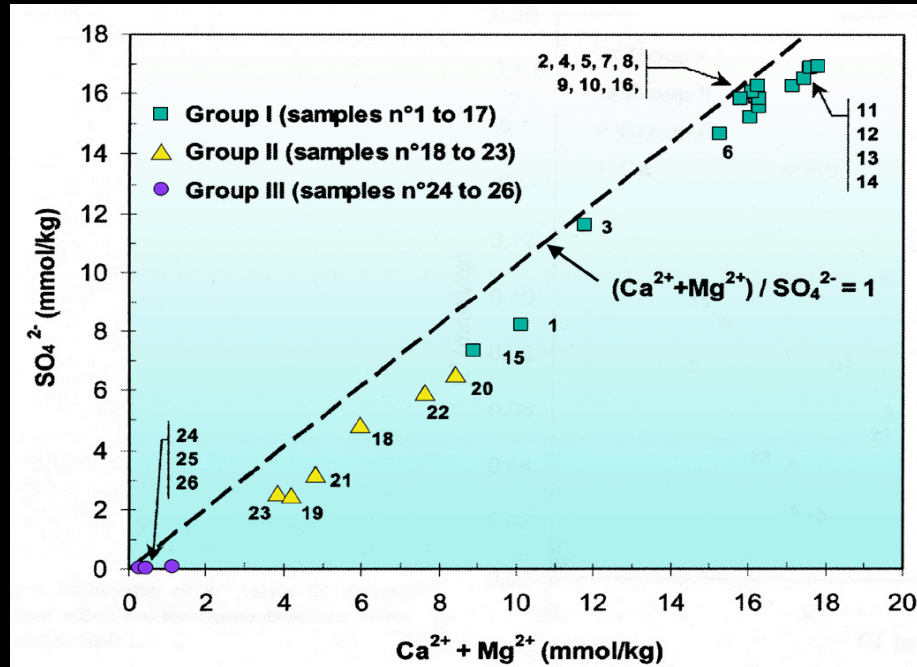
Tipi di acque

Le acque **Na-Cl** circolanti in serbatoi geotermici profondi e di alta entalpia con pH da acidi a neutri ed elevate concentrazioni di SiO_2 , K, Li, B e F, basso Mg. I gas disciolti principali sono CO_2 and H_2S . Tali acque profonde possono giungere sino alla superficie ed essere rilasciate da boiling pools con pH da neutri ad alcalini → diluizioni con acque superficiali. Si ritrovano anche a km di distanza.

Acque **Na- HCO_3** per dissoluzione di CO_2 o condensazione di vapore geotermico in acquiferi poco profondi e privi di O_2 . Prevengono l'ossidazione di H_2S e l'acidità è conferita dalla dissociazione di H_2CO_3 . Parti marginali dominati da acqua di un sistema geotermico.

Acque **Cl- SO_4** acide tipiche di ambienti magmatici in HCl , SO_2 e H_2S , portando alla produzione di soluzioni acide fortemente reattive ed ossidate. Non neutralizzabili per poca roccia a disposizione al contrario di quanto avviene in profondità ove tali acque interagiscono con più roccia portando alla formazione di acque neutre ricche in NaCl.

Source of water solutes



All samples are close to $SO_4/Ca+Mg = 1$:

→ stoichiometric dissolution of sulfate minerals (gypsum, anhydrite)



All samples are close to $Na/Cl = 1$:

→ stoichiometric dissolution of evaporitic minerals (halite) or Na-Cl waters as seen before



Trace elements can be used to ascertain the deep origin of the waters by eliminating the shallow components if mobile alkaline elements (Li, Rb and Cs) are taken into account.

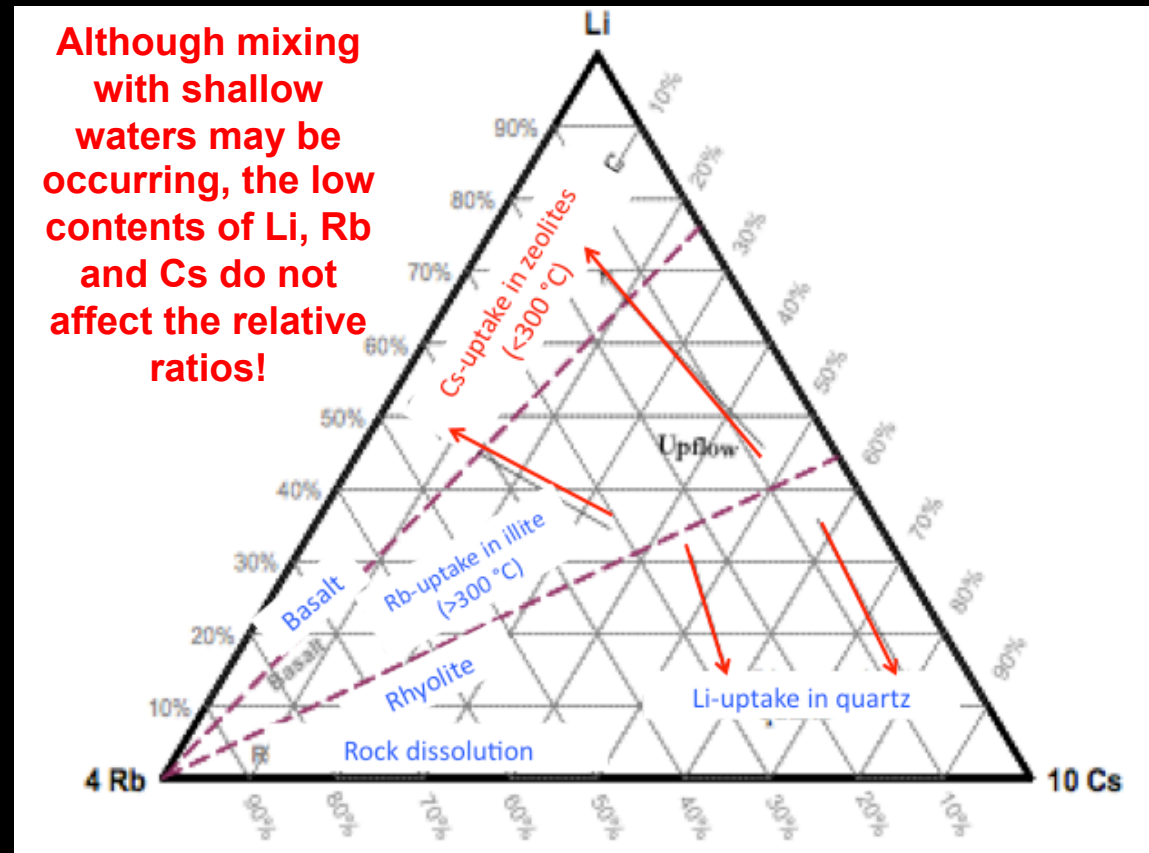
By comparing fresh and altered rhyolites in geothermal wells, Li, Cs and Rb do not seem to be leached but added by dissolution processes of deeper-seated rocks.

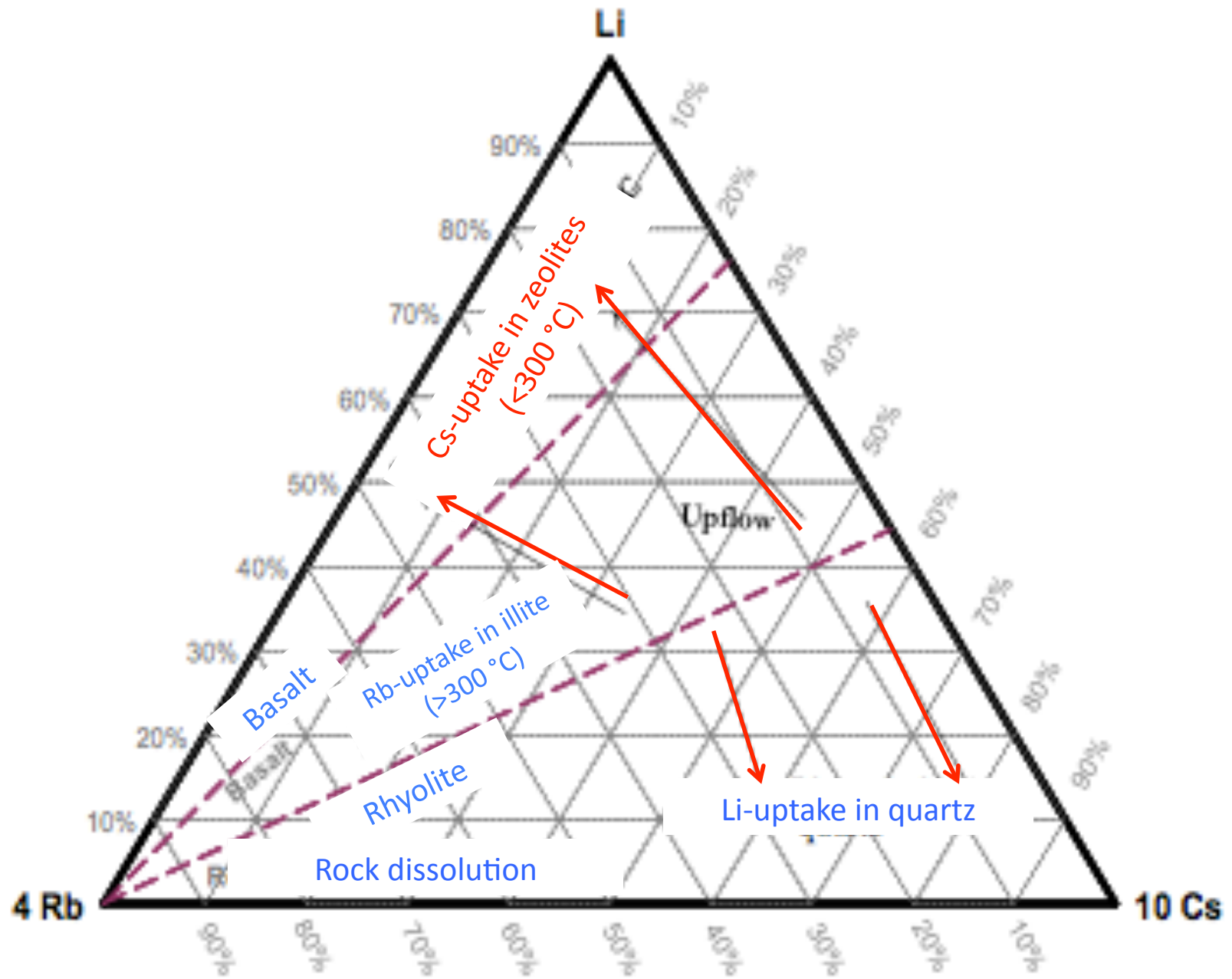
Rb behaves similarly to K and is hosted in K-minerals, e.g. illite:

Cs can enter zeolites at $<250\text{ }^{\circ}\text{C}$.

Li is difficultly hosted, though possible, in quartz and chlorite.

This suggests that Li is more mobile than Rb and Cs...thus...



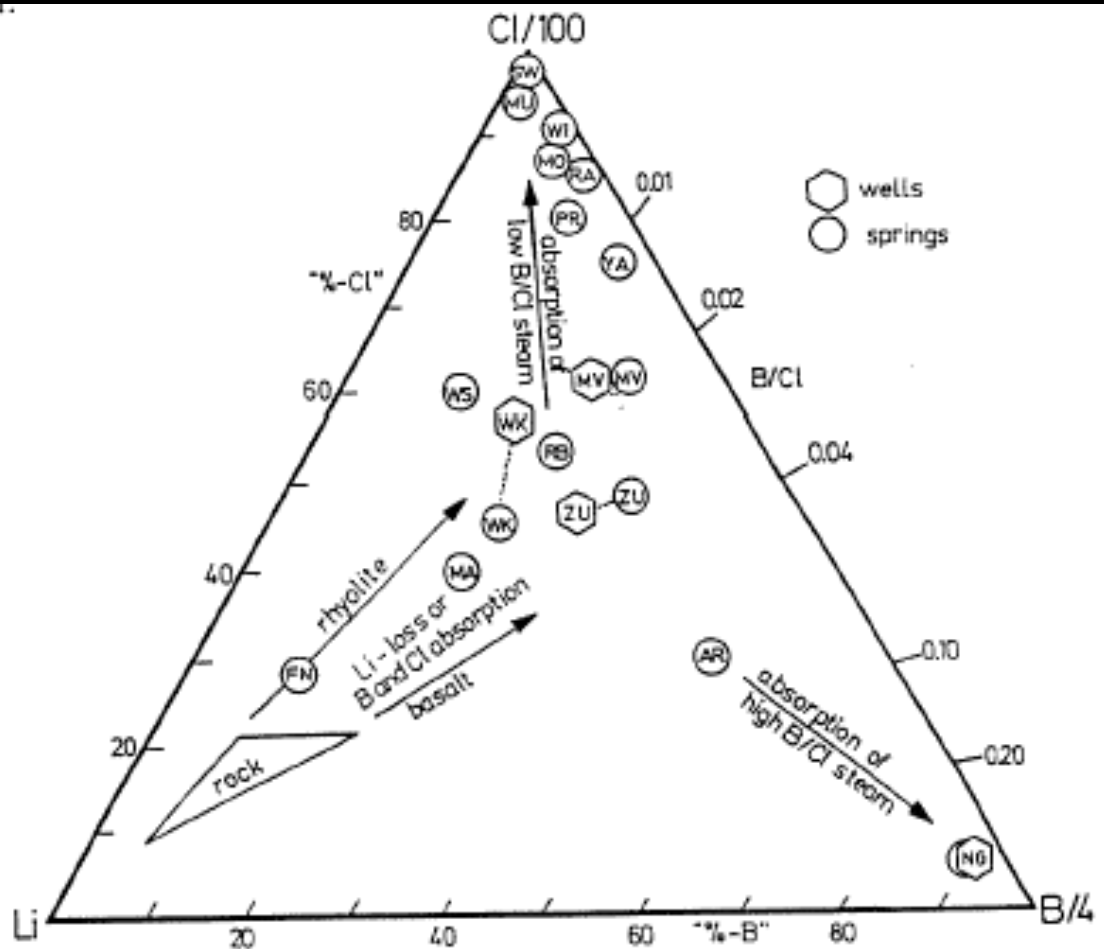


...Li is a good tracer of initial dissolution of altered rocks at depth and it can be coupled with two other mobile (conservative) tracer such as: Cl and B!

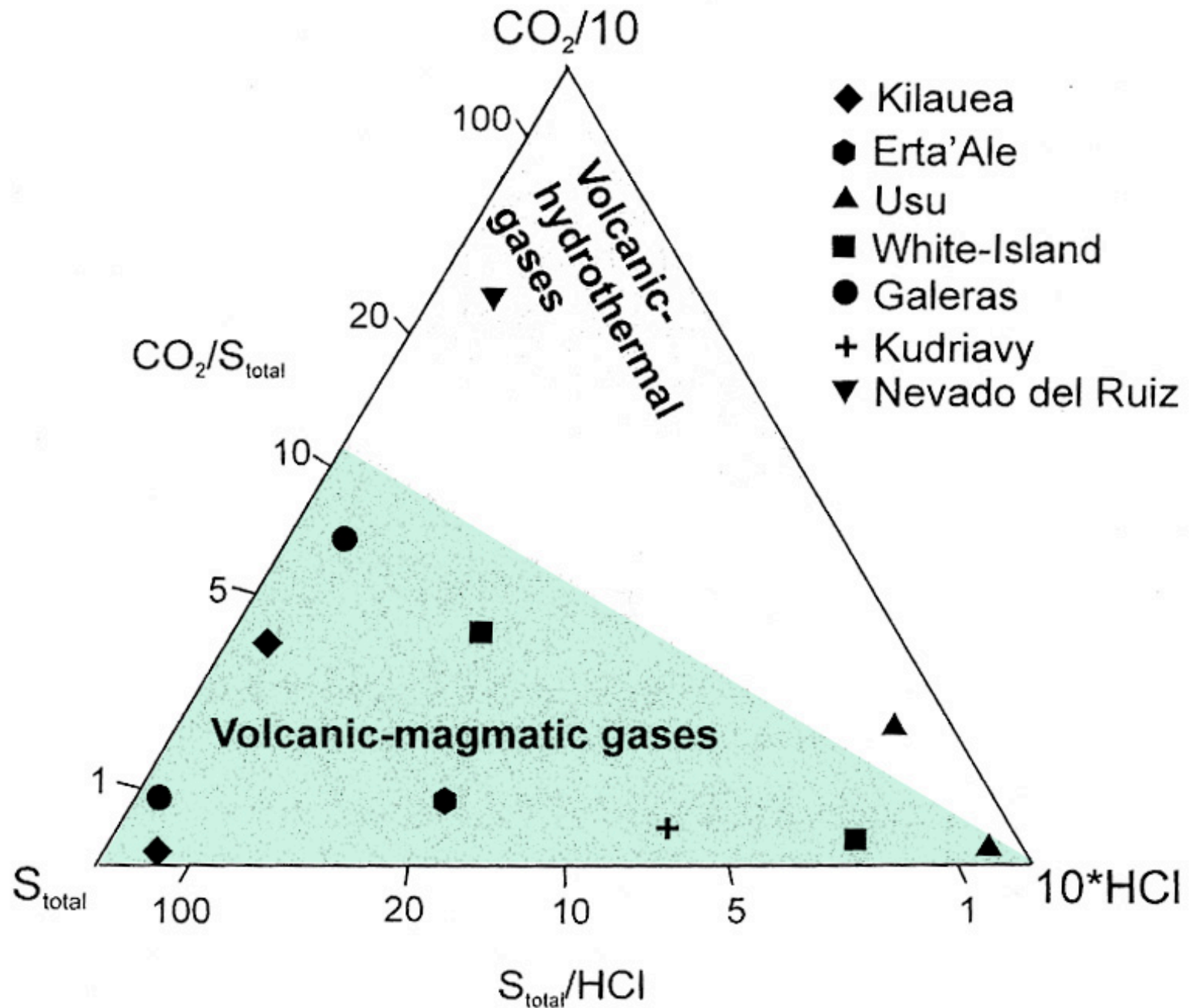
Only one sample is apparently characterized by rock-leaching (FN).

The other samples have higher Cl and B relative contents with respect to that of the rock:

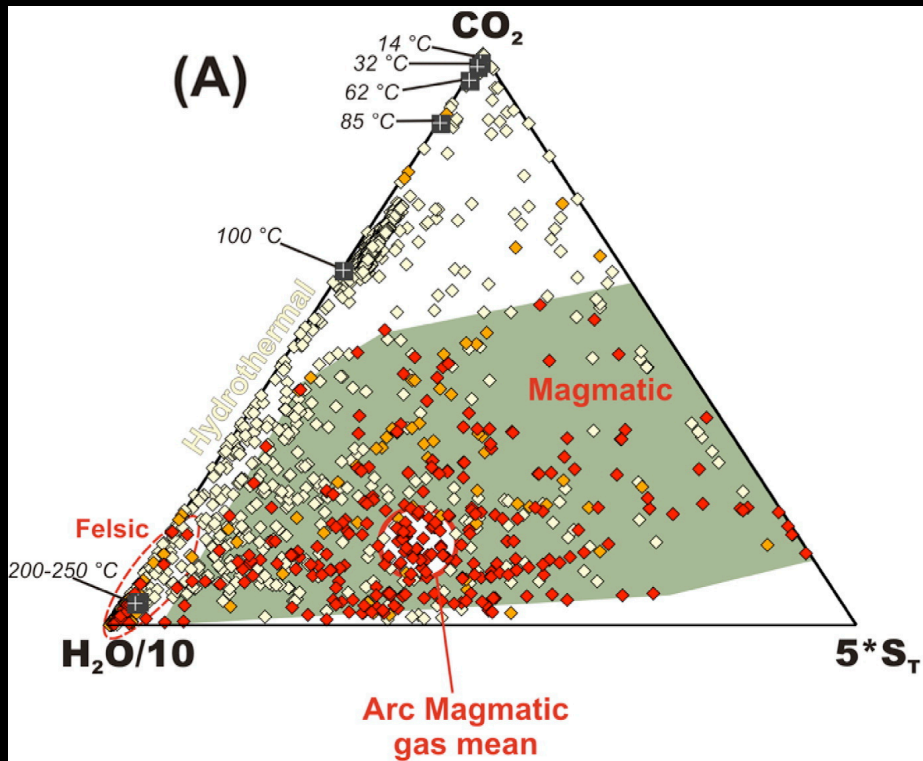
1. Lost of Li. No way! No “hydrothermal sink” of Li;
2. Li stays in solution;
3. Cl and B are added;
4. At HT, Cl is as HCl;
5. At HT, B is as H_3BO_3 ;
6. Both are volatile and can be mobilized by the vapor phase at high T;
7. It can be hypothesized that they were part of the magmatic gases: formation of acidic brines and rock dissolution;
8. At low T, HCl is more acid and consumed by the alteration processes and it forms NaCl waters;
9. Boron prefers the volatile phase and can be carried by the vapor at lower temperatures.



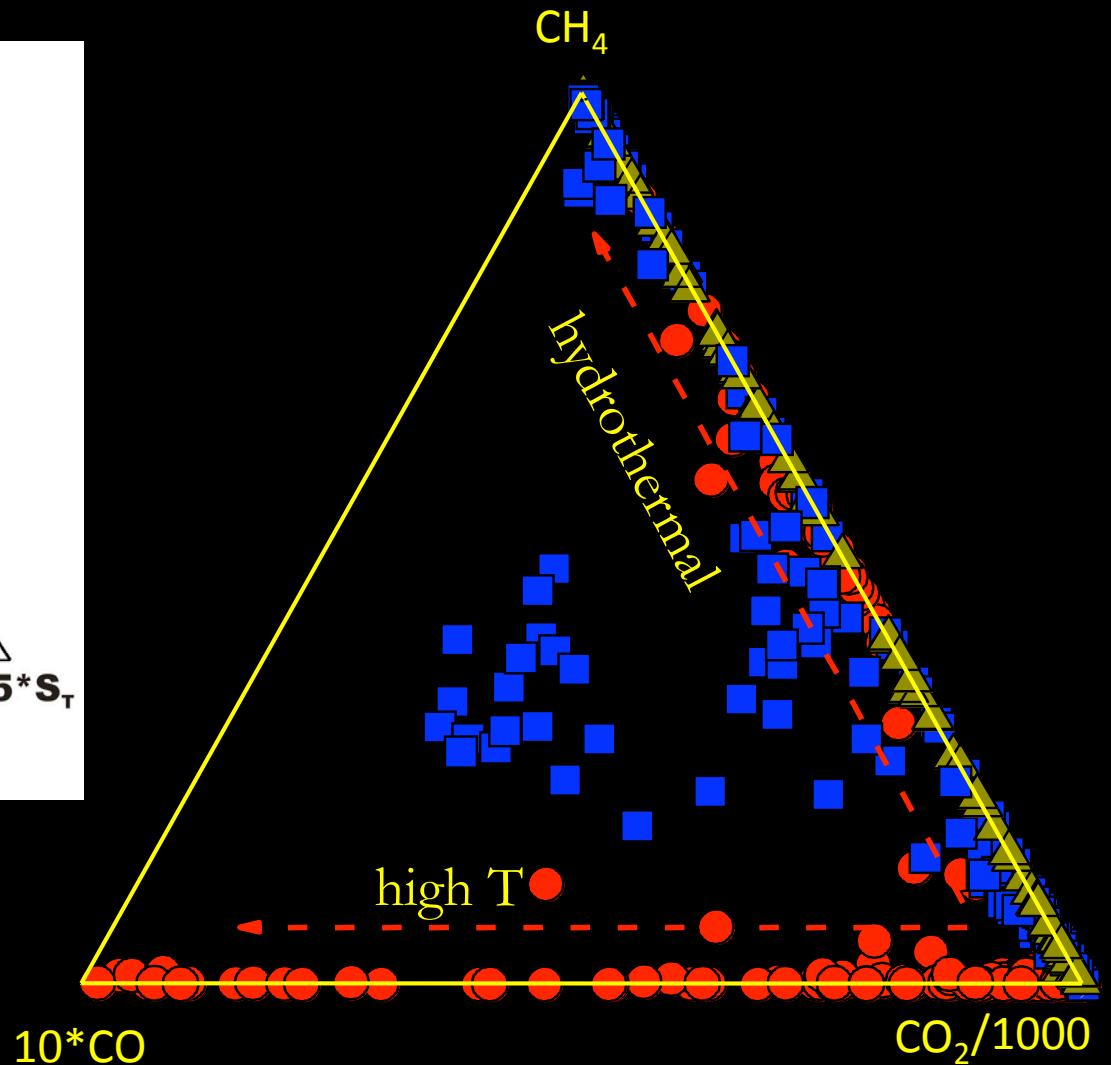
A simple and useful diagram to discriminate the gas sources



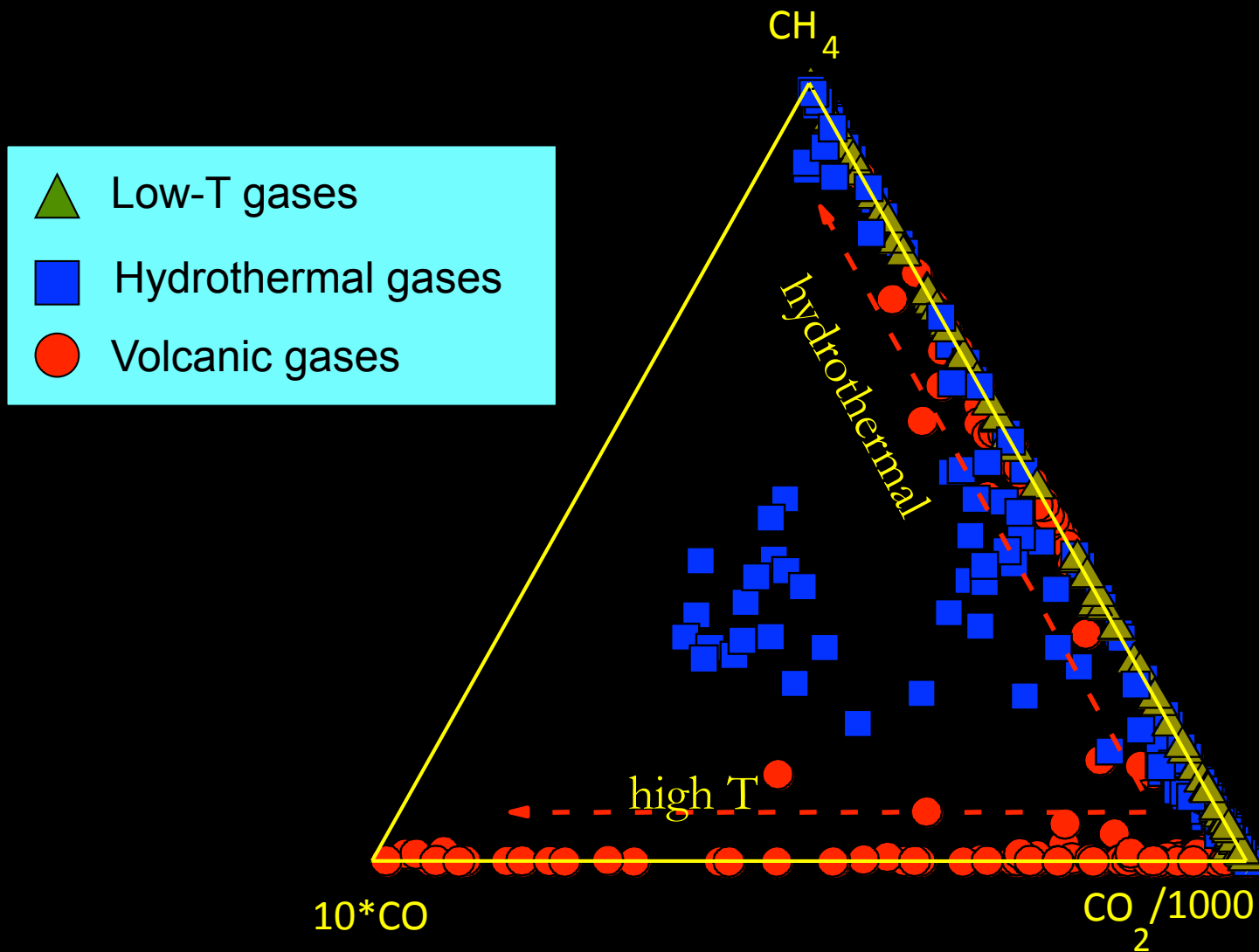
Gas Chemistry: main gases...



- ▲ Low-T gases
- Hydrothermal gases
- Volcanic gases



Carbon gas compounds



I gas inerti: l'origine di N_2 , Ar e He

N_2 : 78.08 %
Ar: 0.93 %

→ $N_2/Ar=83$
AIR

N_2 : 12 mg/L
Ar: 0.315 mg/L

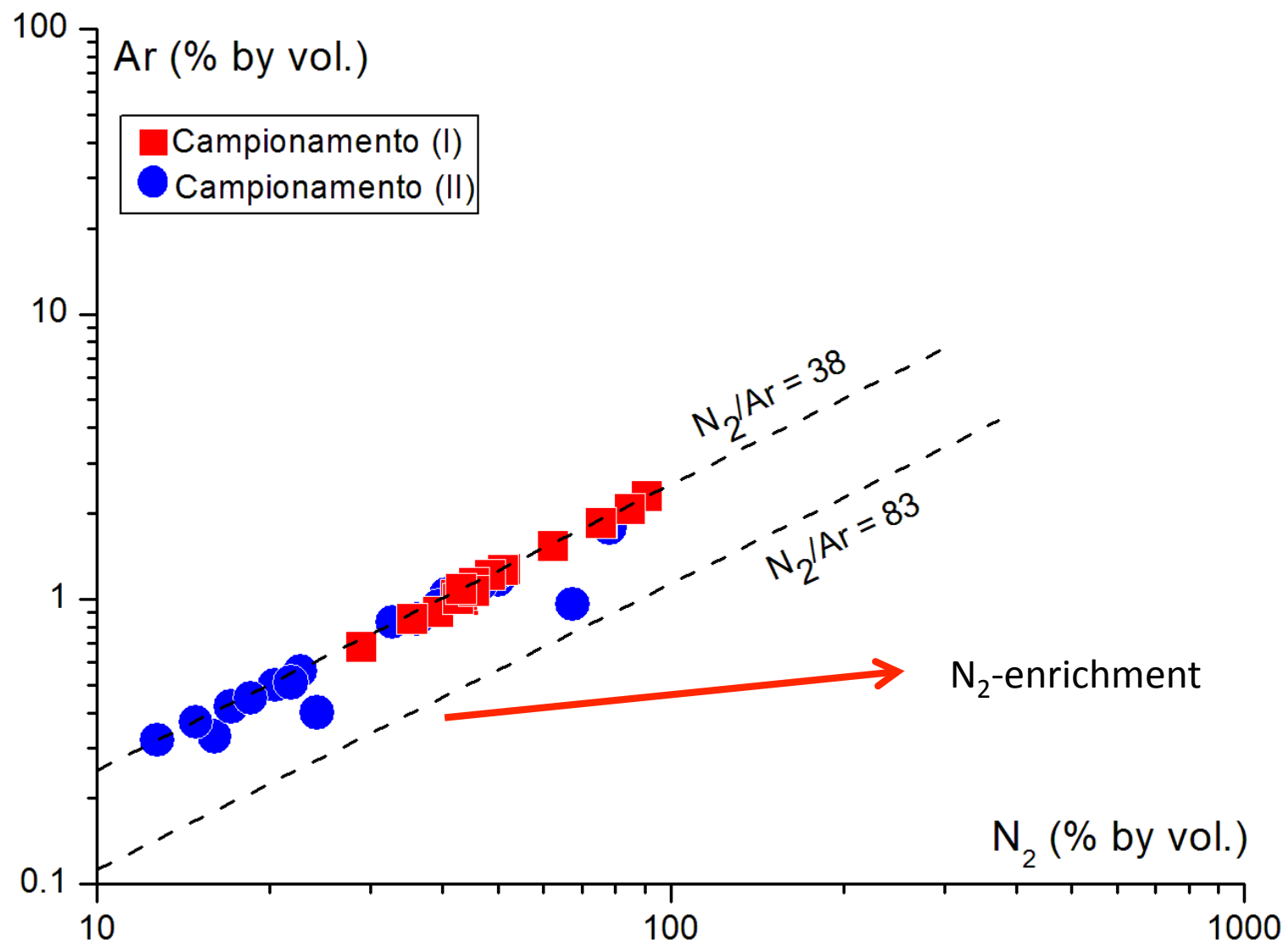
→ $N_2/Ar=38$
ASW

Relazioni fra alcuni gas di derivazione atmosferica

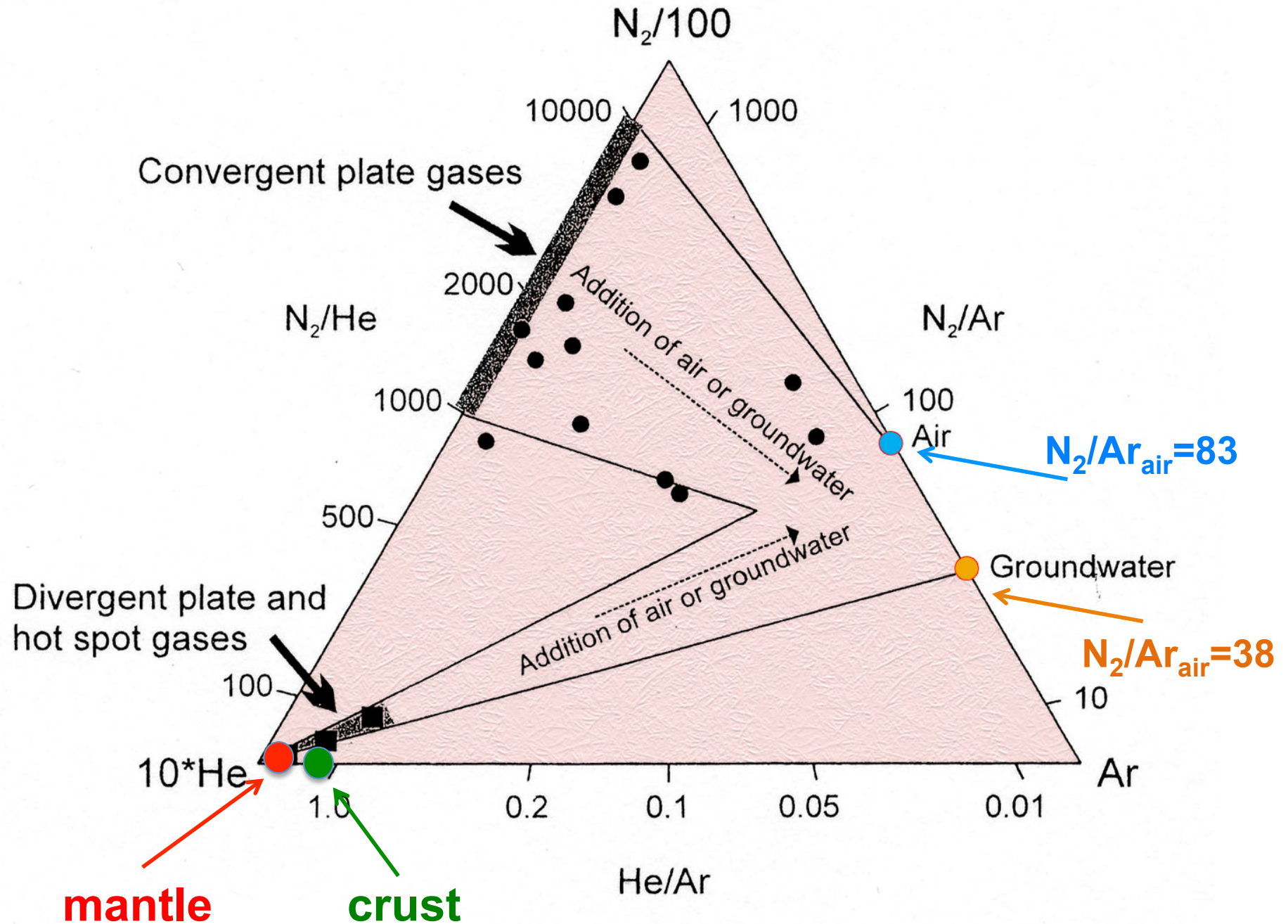
Quali sono i rapporti che dobbiamo considerare?

T °C	N ₂ /Ar	N₂/O₂	He/Ar	Ne/Ar	He/Ne	N ₂ /He	N ₂ /Ne	O₂/Ar	O₂/Ne	O₂/He
10	37.50	1.84	0.0001	0.0005	0.231	300008	69575	20.3699	37792	162959
20	38.37	1.88	0.0001	0.0006	0.246	262788	64482	20.408	34299.1	139781
30	38.94	1.91	0.0002	0.0007	0.254	225058	57342	20.3422	29959.1	117585
40	39.44	1.95	0.0002	0.0007	0.266	200183	53077	20.2444	27246.8	102763
50	39.87	1.98	0.0002	0.0008	0.271	183733	49838	20.116	25145.1	92700.7
60	40.20	2.02	0.0002	0.0009	0.268	162765	43651	19.9123	21620.3	80616.7
70	40.48	2.06	0.0003	0.0010	0.267	153326	40928	19.6782	19897	74538.5
Aria	83.60	3.73	0.0006	0.0020	0.288	149015	42950	22.4254	11521.5	39973.3
T °C	N ₂ /Ar	N ₂ /O ₂	N ₂ /Ne	O ₂ /Ar	O ₂ /Ne					
20	38.37	1.88	64482	20.4	34299					
Air	83.6	3.73	42950	22.4	11521					

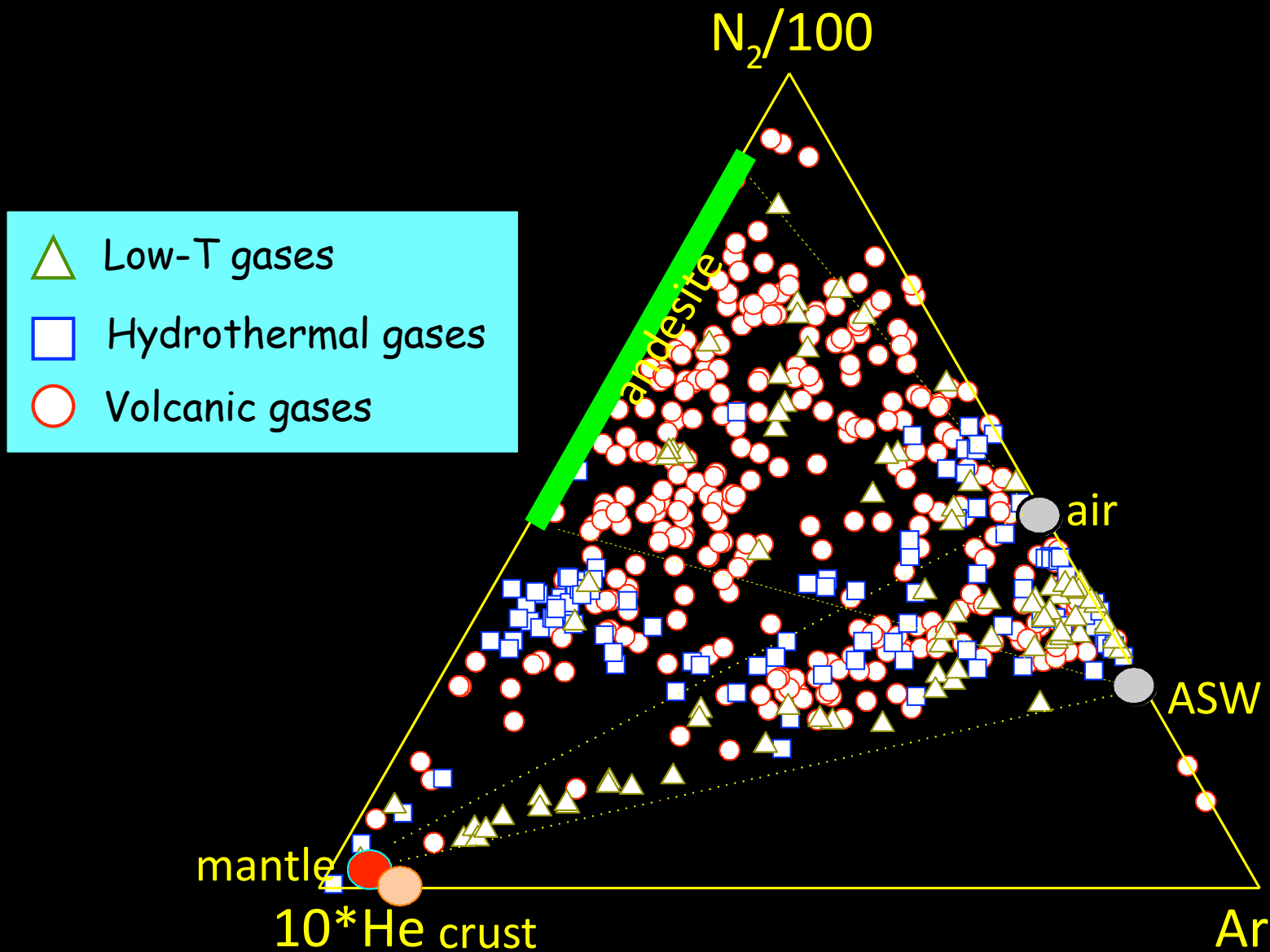
Posso avere rapporti più elevati di N₂/Ar?



...and to discriminate the noble gases...



Inert gases



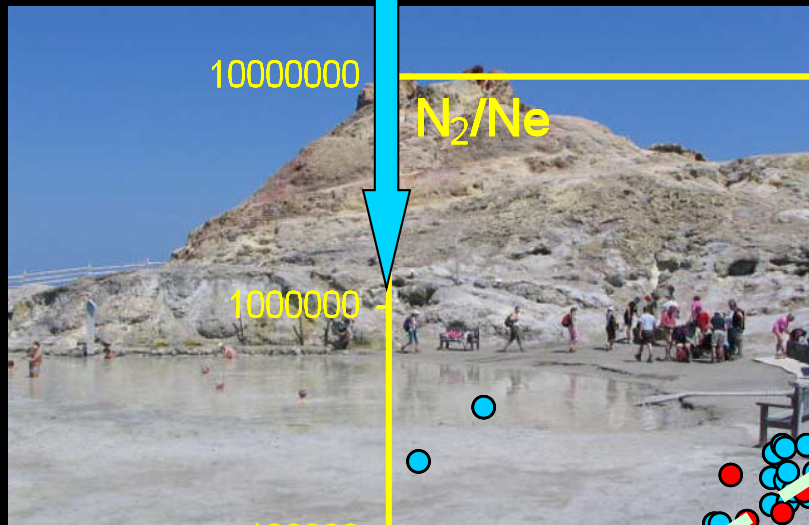


Campo fumarolico di alta temperatura

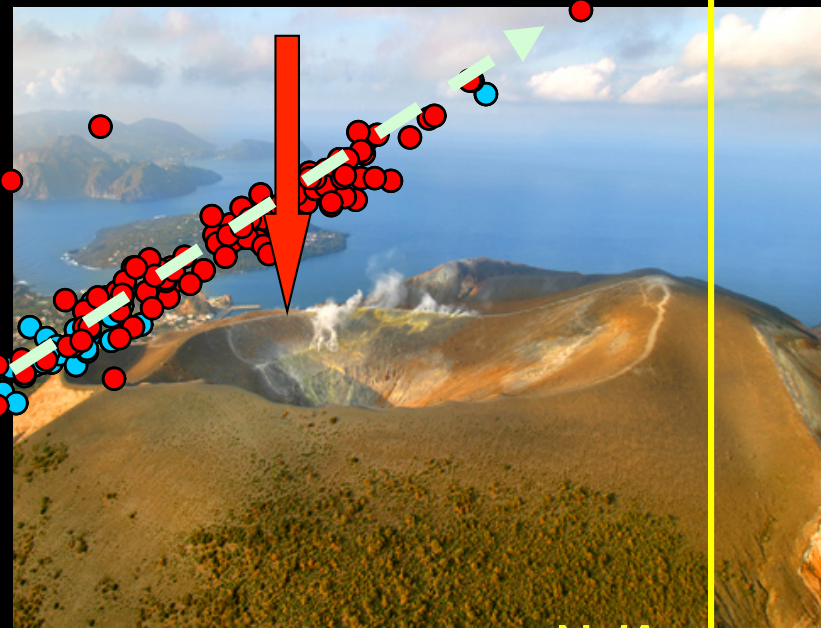
Campo fumarolico di bassa temperatura



Gas di bassa T: bubbling gases (Baia di Levante)



Gas di alta T (fumarole)



10000000

N_2/Ne

1000000

100000

air saturated water^{air}

N_2/Ar

10000

10

100

1000

10000

È presente una elevata quantità di N_2 non atmosferico che si definisce come: N_2 -excess

Isotopi stabili dell'azoto

Abbondanze dei due isotopi stabili

$^{14}\text{N} = 99.64\%$

$^{15}\text{N} = 0.36\%$

La notazione delta

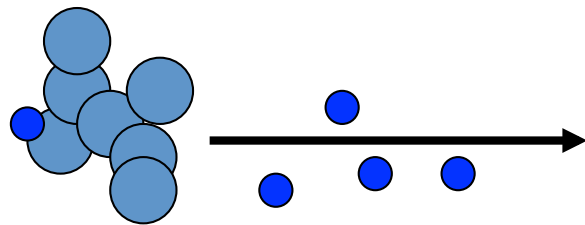
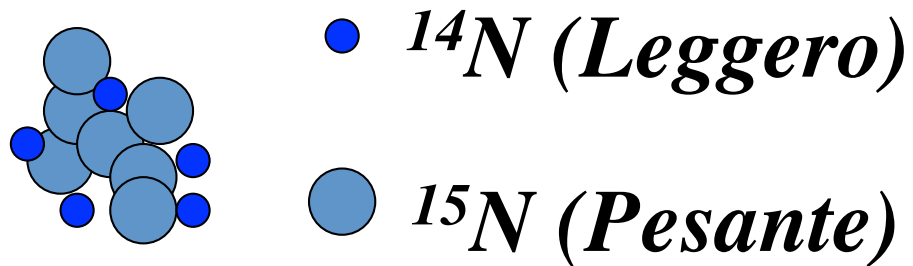
Per gli isotopi stabili si usa il rapporto sulla base della loro abbondanza! </>

$$\delta^{15}\text{N}\text{‰} = \frac{(^{15}\text{N}/^{14}\text{N}_{(\text{campione})} - ^{15}\text{N}/^{14}\text{N}_{(\text{Air})\text{NBS}})}{(^{15}\text{N}/^{14}\text{N}_{(\text{Air})\text{NBS}})} * 1000$$

National Bureau Standard

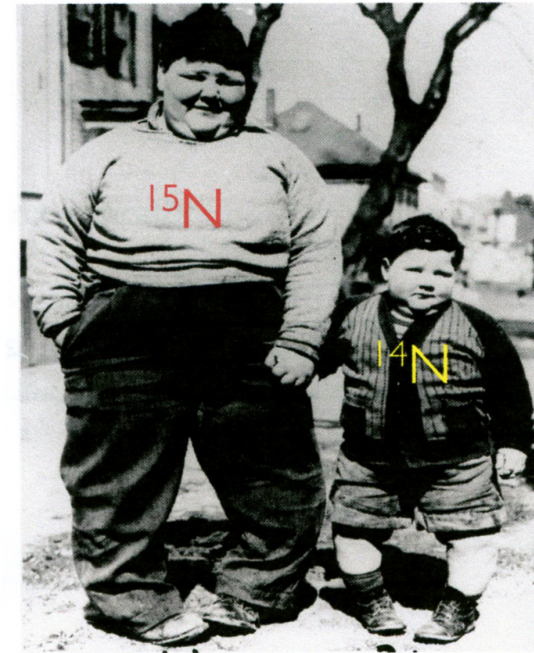
Isotopi Stabili

Il frazionamento isotopico è controllato dalle forze di legame e segue la regola generale per la quale gli isotopi leggeri tendono a formare legami più deboli di quelli pesanti.



Frazionamento

Processi chimici e biologici differenziano gli isotopi leggeri da quelli pesanti



Variazione nel valore $\delta^{15}\text{N}$

Table 27.1 Average concentrations of nitrogen in terrestrial and extraterrestrial rocks (Wlotzka, 1972)

	<i>Nitrogen, ppm</i>
Meteorites	
carbonaceous chondrites	1850
enstatite chondrites with sinoite	708
enstatite chondrites without sinoite	220
all other chondrites	40
achondrites	38
iron meteorites	72
Lunar rocks (basalt, breccia and fines)	106
Minerals	
muscovite	68
biotite	55
K-feldspar	23
plagioclase	22
hornblende	18
quartz	13
pyroxene	11
Granites and granodiorites	21
Gabbros and diorites	11
Ultramafic rocks	14
Rhyolites and obsidian	28
Phonolites and trachytes	36
Andesites	87
Basalt	30
Shale	602
Greywacke	180
Sandstone	120
Carbonate rocks	73
Chert	210
Modern marine sediment	1772
Coal	2,000–30,000
Petroleum	100–20,000
Natural gas	variable, up to 90% by volume


Concentrazioni medie di azoto nelle rocce terrestri e extraterrestri

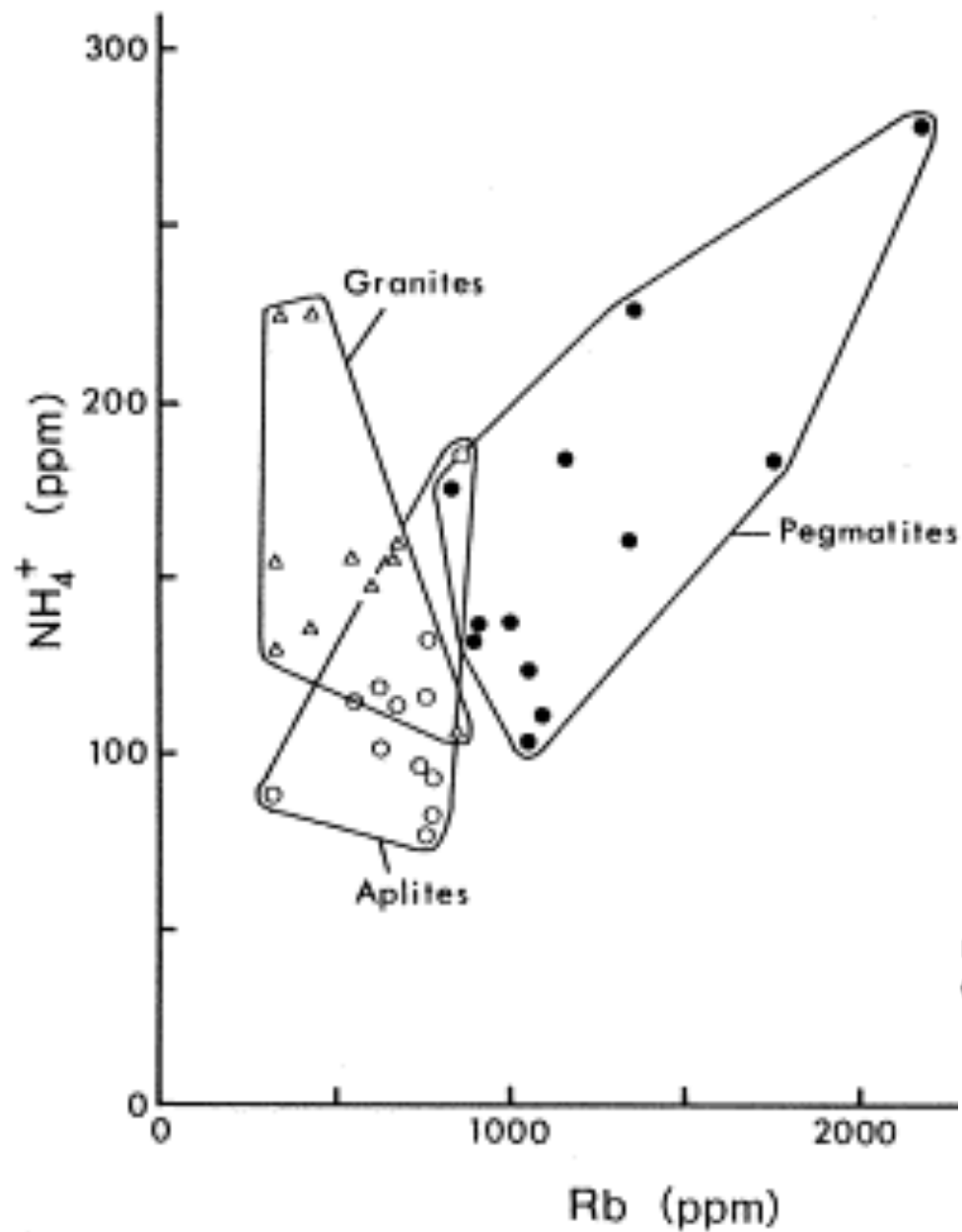
Il maggior serbatoio di azoto è l'atmosfera dove è presente nella forma



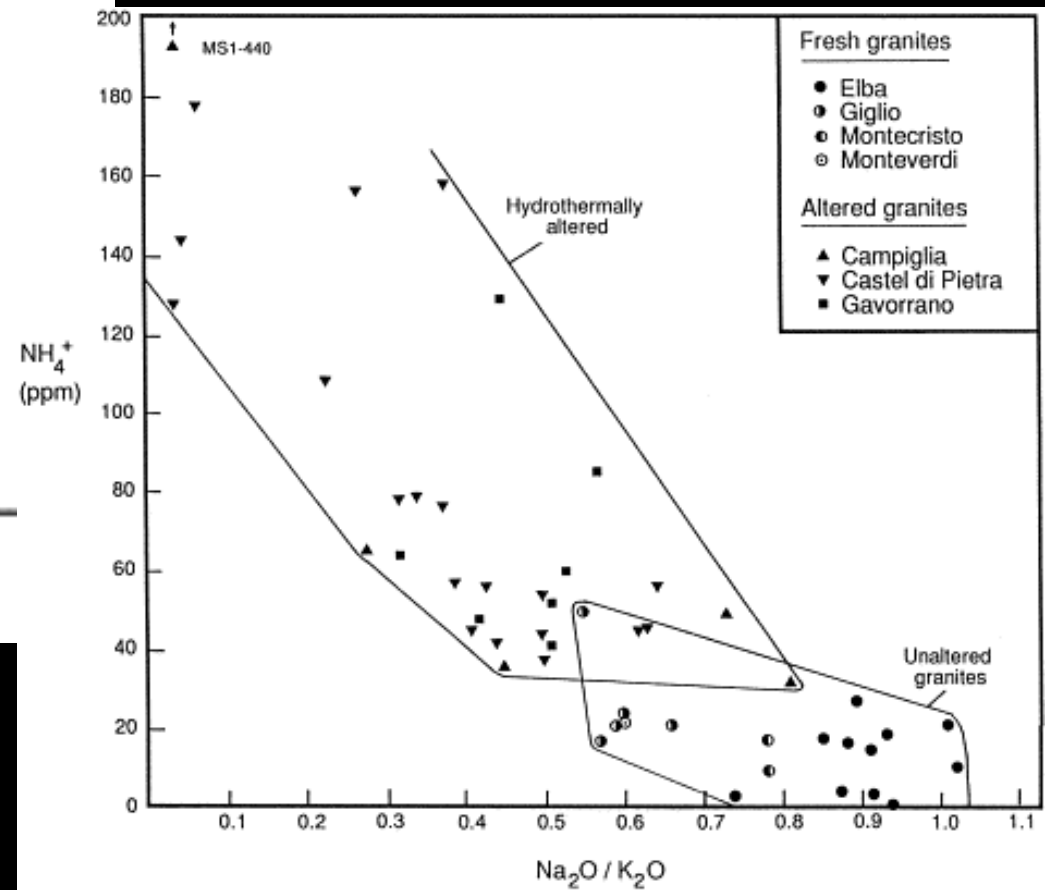
con circa il 78% in vol.

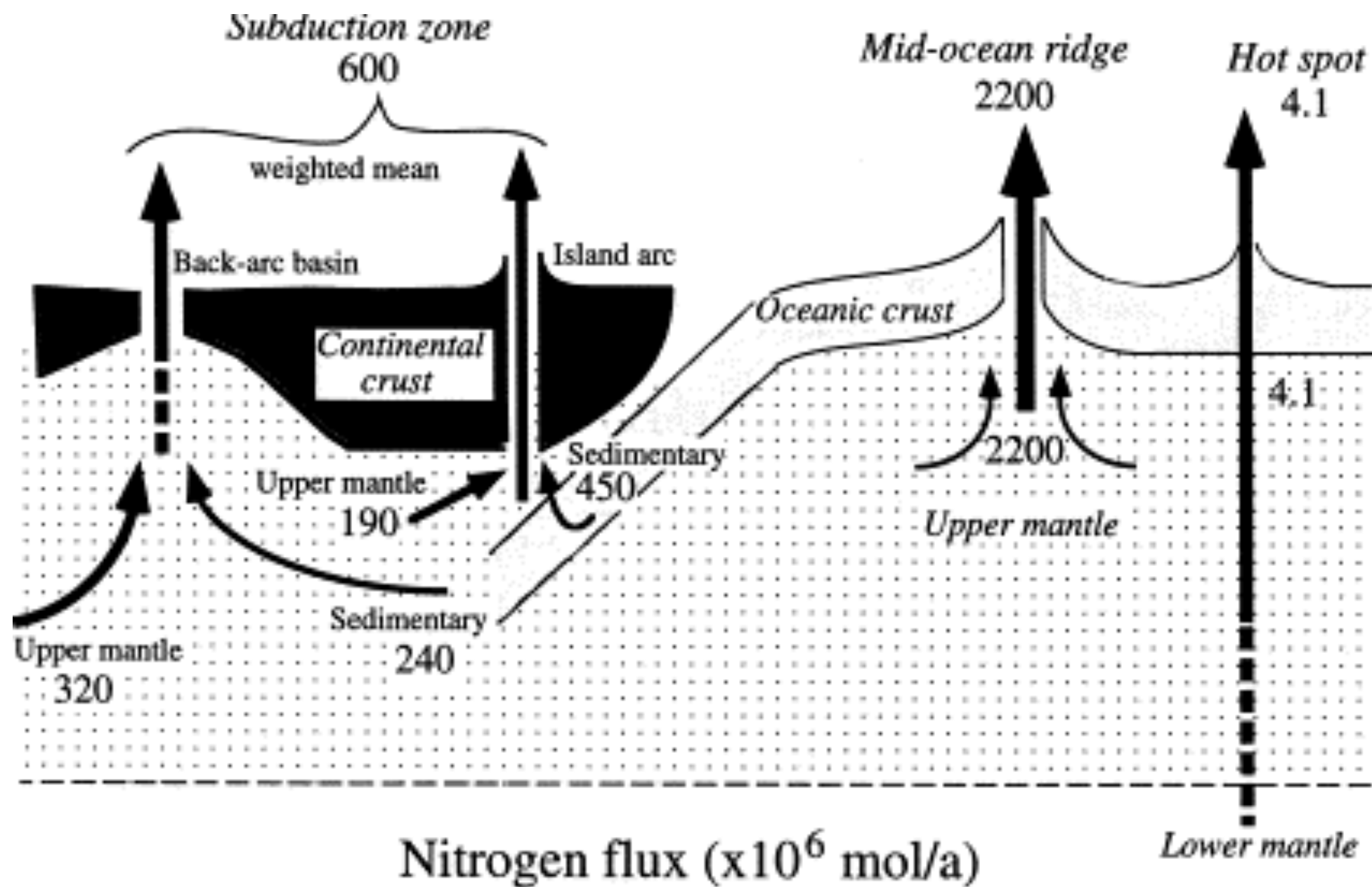
Come si ritrova l'Azoto nelle rocce?


 NH_4^+ come sostituyente isomorfo di K^+ o dentro inclusioni fluide come N_2



1.45 Å (NH_4) contro 1.33 Å (K)
e 1.49 (Rb) Å





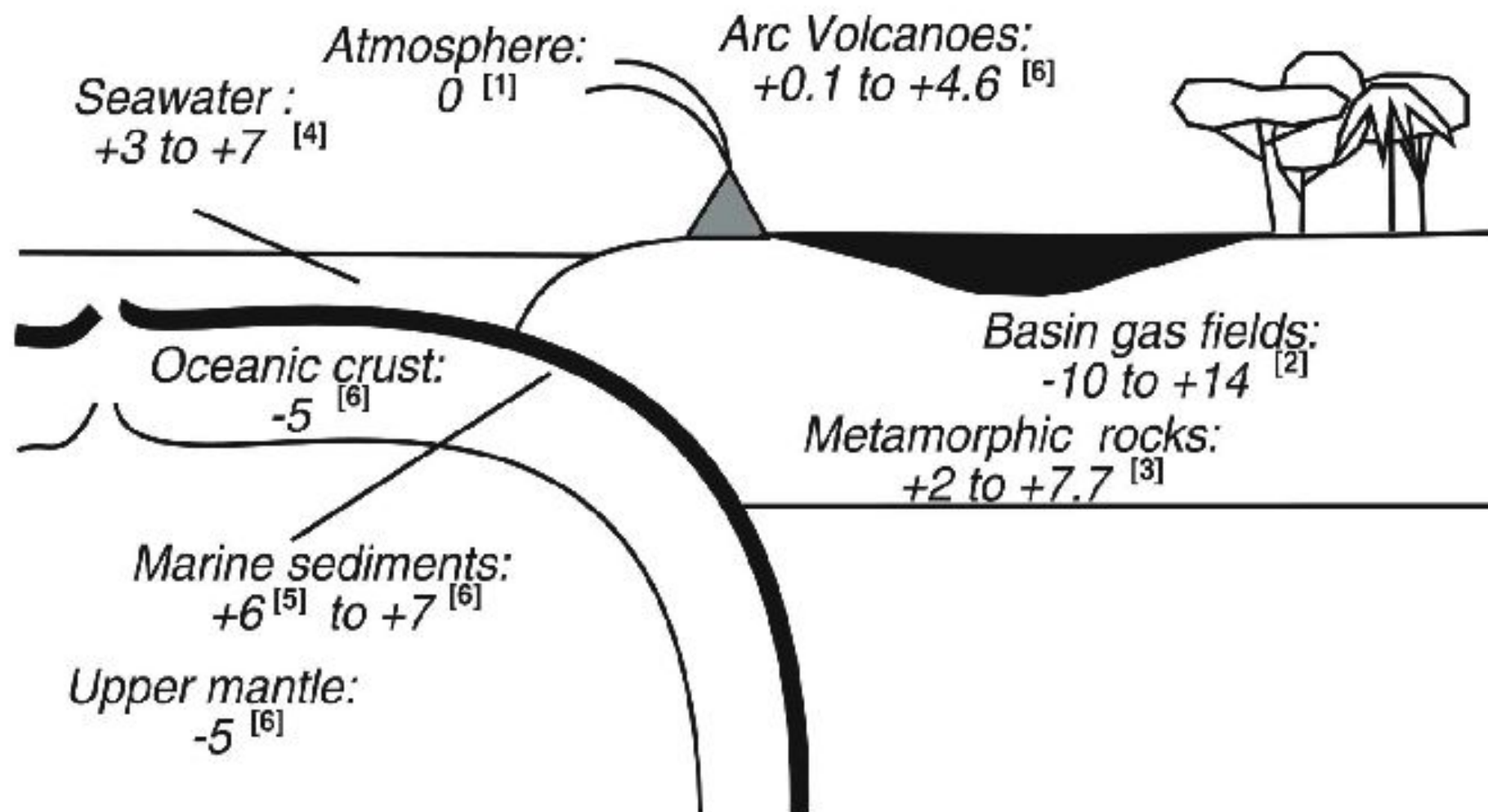
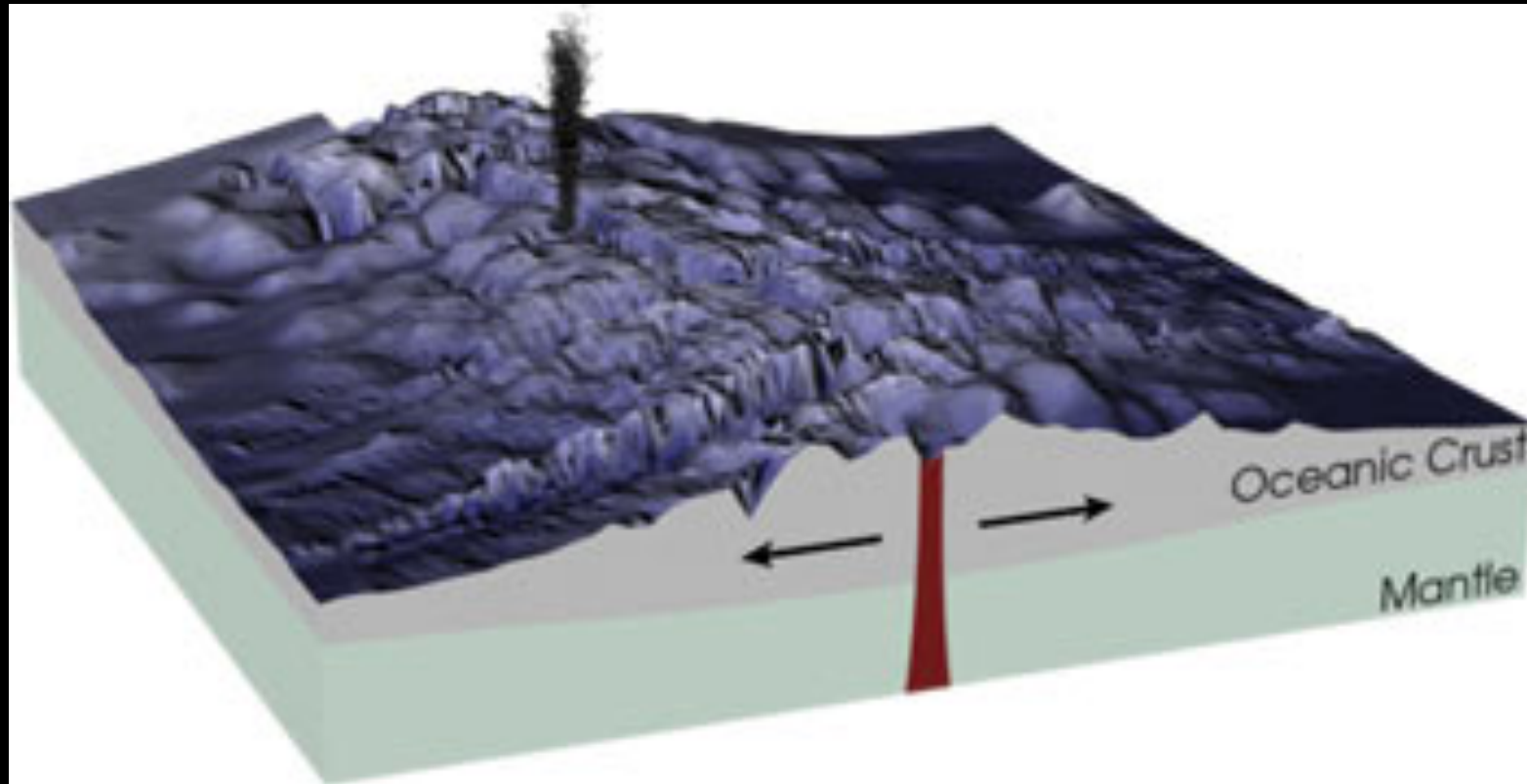


Figure 4. Representative values of $\delta^{15}\text{N}$ for nitrogen in crustal and upper mantle reservoirs. Atmospheric standard (1); Zhu *et al.* [2000] (2); Mingram and Bräuer [2001] (3); Bickert [2000] (4); Boyd [2001] (5); Sano *et al.* [2001] (6).

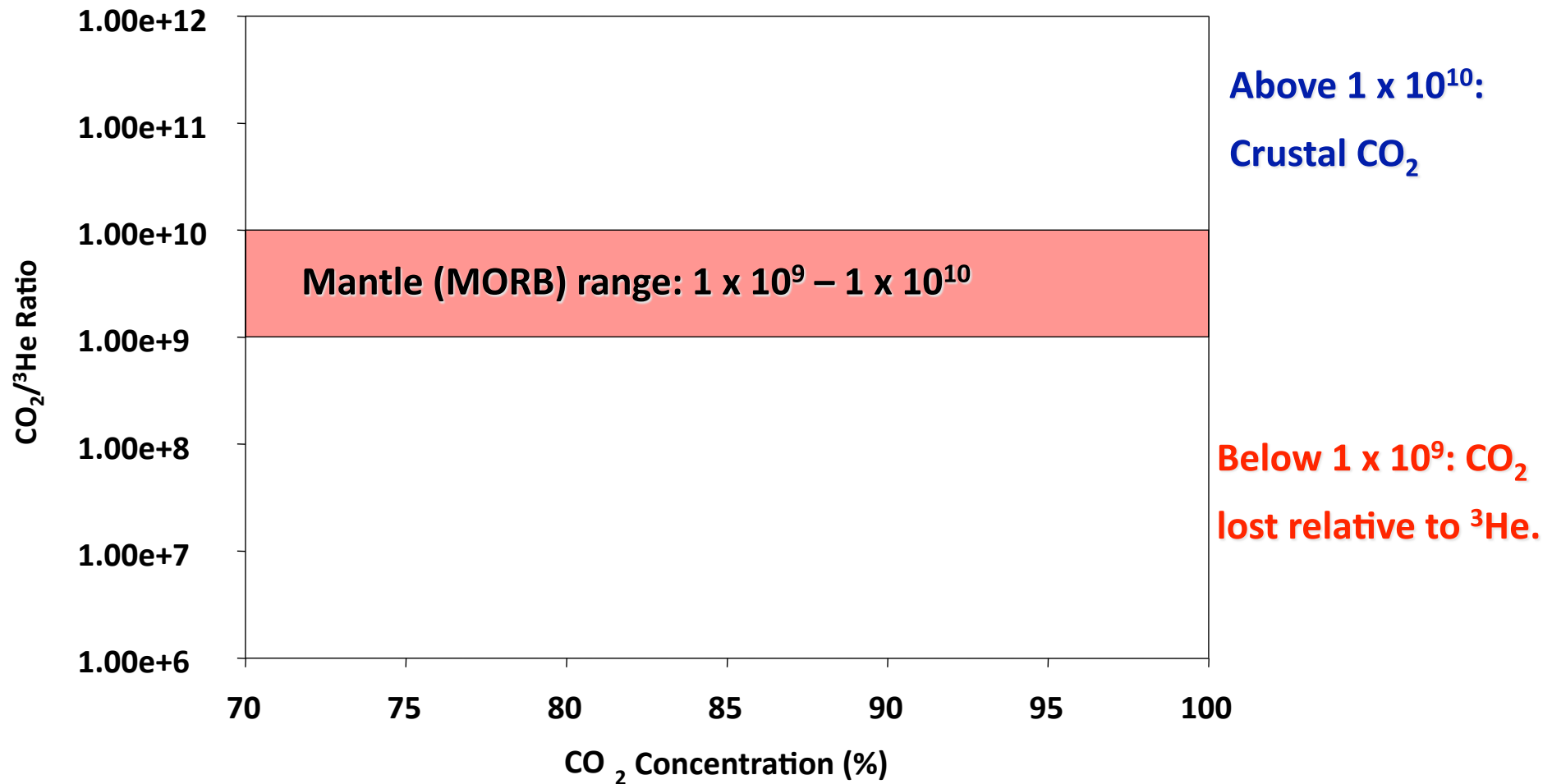
arc systems [*Sano et al.*, 2001]. The upper mantle and the oceanic crust yield isotopically light $\delta^{15}\text{N}$ values of -6‰ relative to air standard, while some surface reservoirs have positive $\delta^{15}\text{N}$ values (Figure 4). The fact that volcanic gases nearly always present positive $\delta^{15}\text{N}$ values, while back arc basin volcanic glasses often have slightly negative $\delta^{15}\text{N}$ values, has been cited as evidence that fumaroles release recycled nitrogen derived predominantly from subducted sources. Values of $\delta^{15}\text{N}$ for a variety of arc gases and fluids range from -0.1 to $+4.6$ [*Sano et al.*, 2001]. It must be noted, however, that systematic variations in $\delta^{15}\text{N}$ values may also be a result of the release of crustal nitrogen, which has undergone varying degrees of metamorphic alteration. The degree of metamorphism on sedimentary rocks has a strong effect on $\delta^{15}\text{N}$ due to the preferential release of ^{14}N -rich ammonium during low-grade metamorphism. Slates and other low-grade metasediments typically have $\delta^{15}\text{N}$ values of $+1$ to $+3$, mica schists from $+2$ to $+5$, and gneisses from $+5$ to $+11$ [*Mingram and Bräuer*, 2001]. Molecular nitrogen in natural gas fields also displays large variations with increasing thermal maturity of organic matter.

Origin of the $\text{CO}_2 - \text{CO}_2/{}^3\text{He}$ ratio

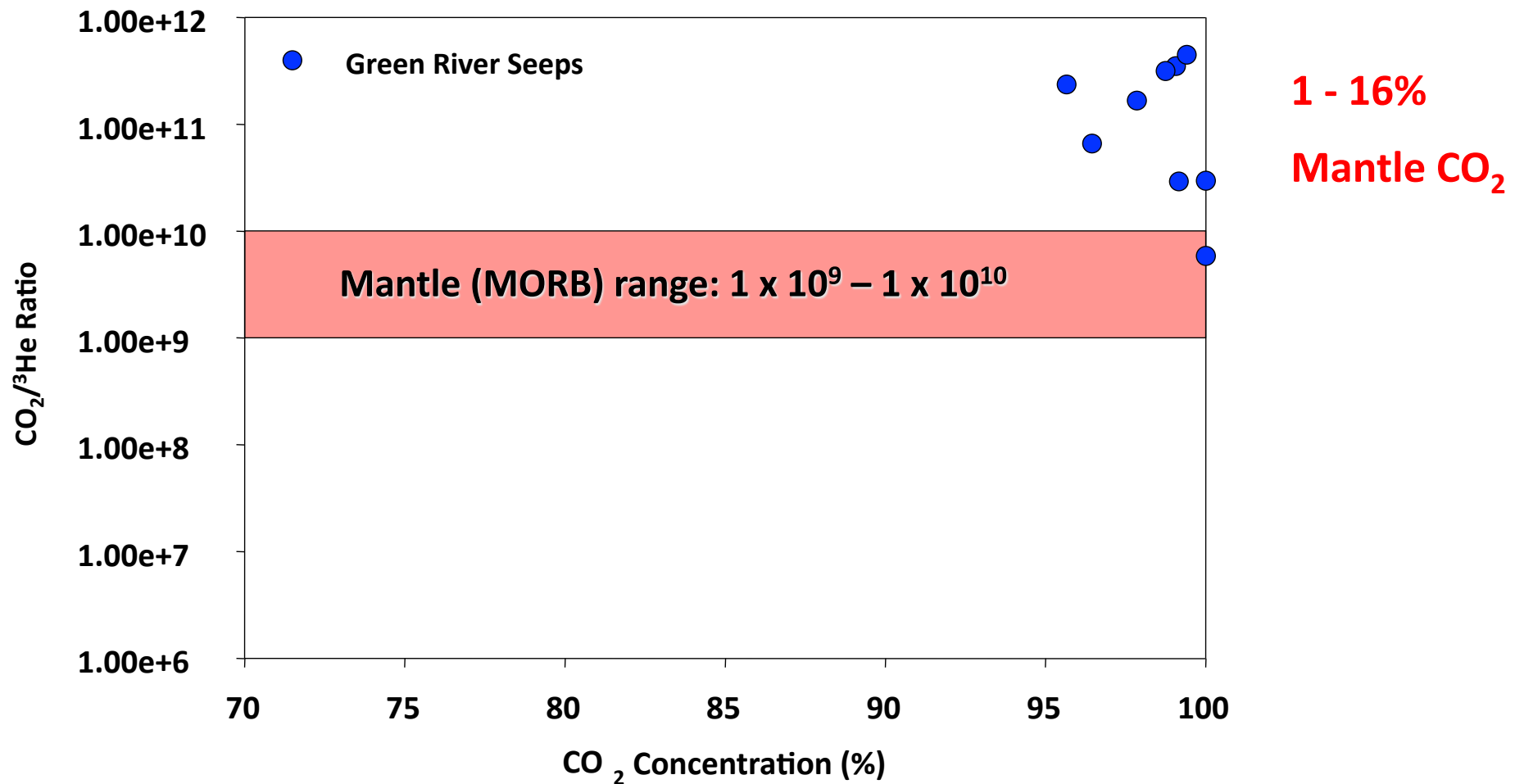


- Mantle $\text{CO}_2/{}^3\text{He}$ range: $1 \times 10^9 - 1 \times 10^{10}$
- Measured from Mid Ocean Ridge Basalts - MORBs

Origin of the $\text{CO}_2 - \text{CO}_2/{}^3\text{He}$ ratio



Origin of the CO₂ – CO₂/³He ratio



- Predominantly crustal derived CO₂ erupted from the Green River seeps.
- Small mantle component → 1 – 16%

$$M + L + S = 1$$

M: mantle degassing; L: limestone; S organic-rich sediments.

$$(\delta^{13}\text{C-CO}_2)_{\text{obs}} = M(\delta^{13}\text{C-CO}_2)_{\text{MORB}} + L(\delta^{13}\text{C-CO}_2)_{\text{Lim}} + S(\delta^{13}\text{C-CO}_2)_{\text{Sed}}$$

$$\left(\frac{1}{\text{CO}_2/{}^3\text{He}}\right)_{\text{obs}} = \left(\frac{M}{\text{CO}_2/{}^3\text{He}}\right)_{\text{MORB}} + \left(\frac{L}{\text{CO}_2/{}^3\text{He}}\right)_{\text{Lim}} + \left(\frac{S}{\text{CO}_2/{}^3\text{He}}\right)_{\text{Sed}}$$

$$(\delta^{13}\text{C-CO}_2)_{\text{MORB}} = -6.5 \text{ ‰}$$

$$(\text{CO}_2/{}^3\text{He})_{\text{MORB}} = 1.5 \times 10^9$$

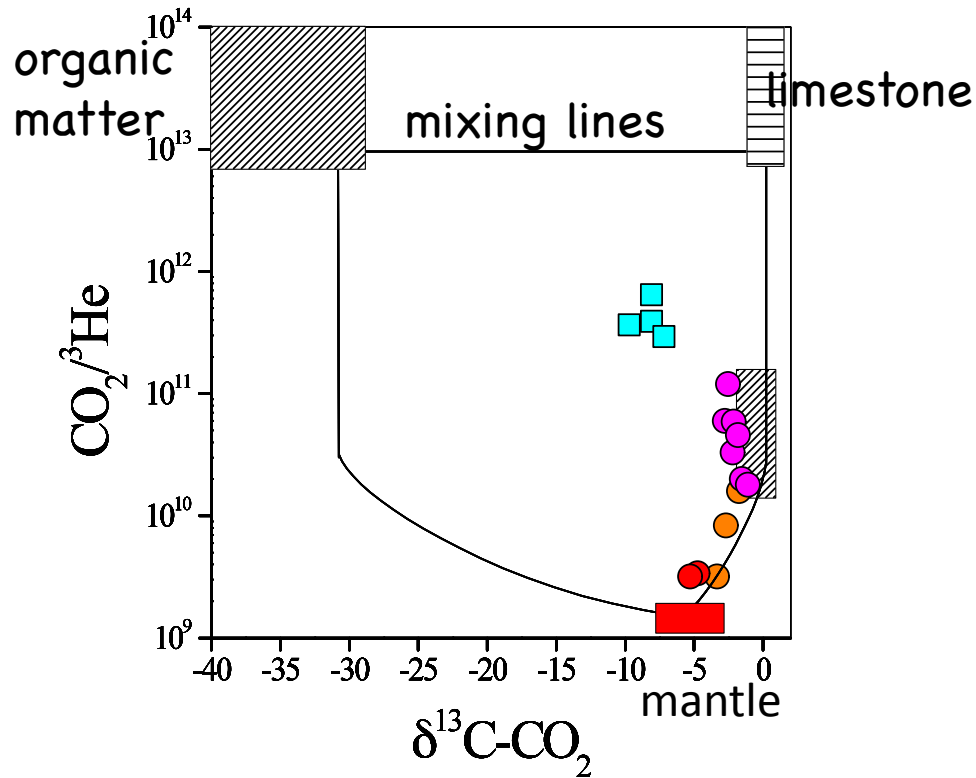
$$(\delta^{13}\text{C-CO}_2)_{\text{Sed}} = -30 \text{ ‰}$$

$$(\text{CO}_2/{}^3\text{He})_{\text{Sed}} = 1.5 \times 10^{13}$$

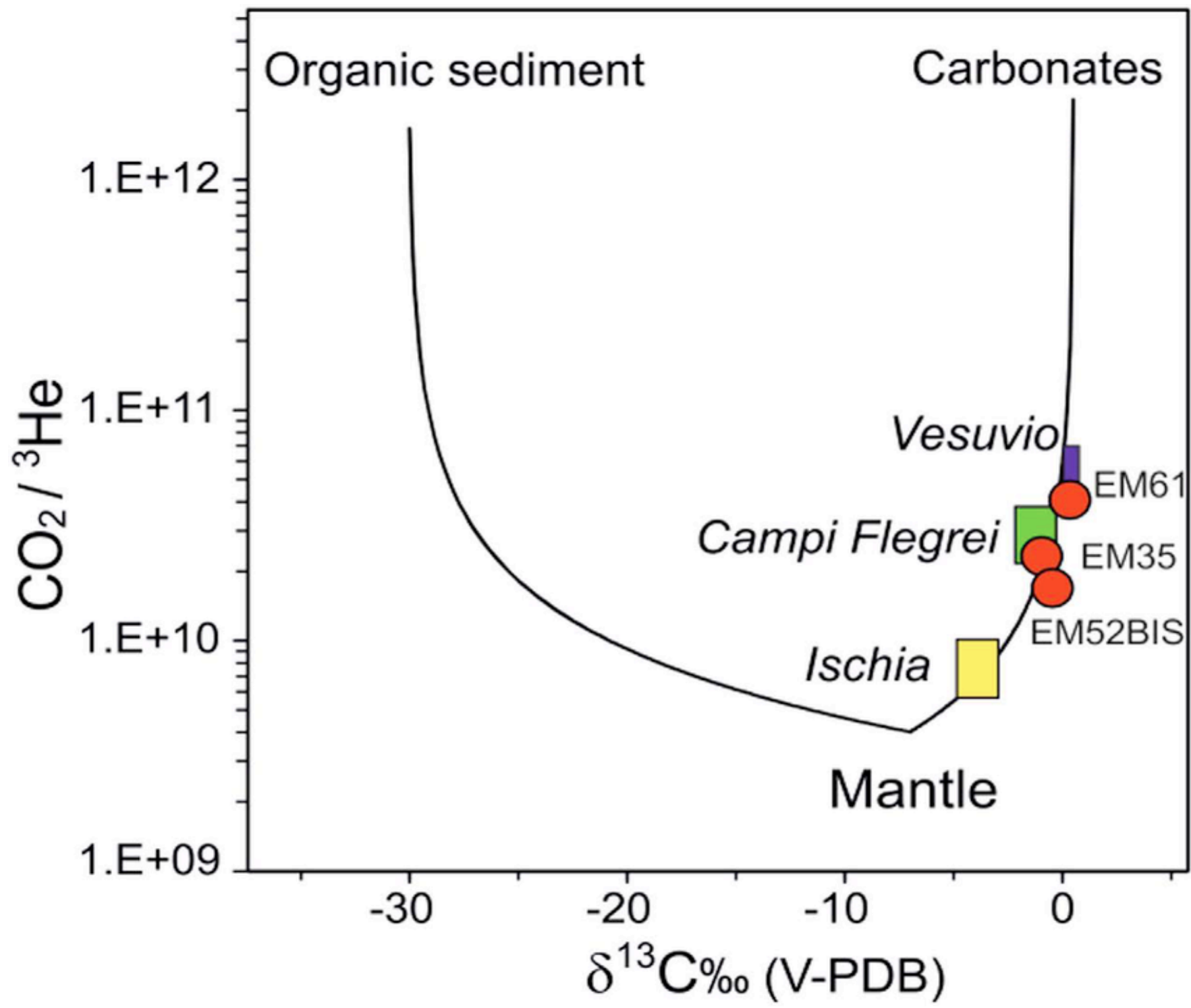
$$(\delta^{13}\text{C-CO}_2)_{\text{Lim}} = 0.0 \text{ ‰}$$

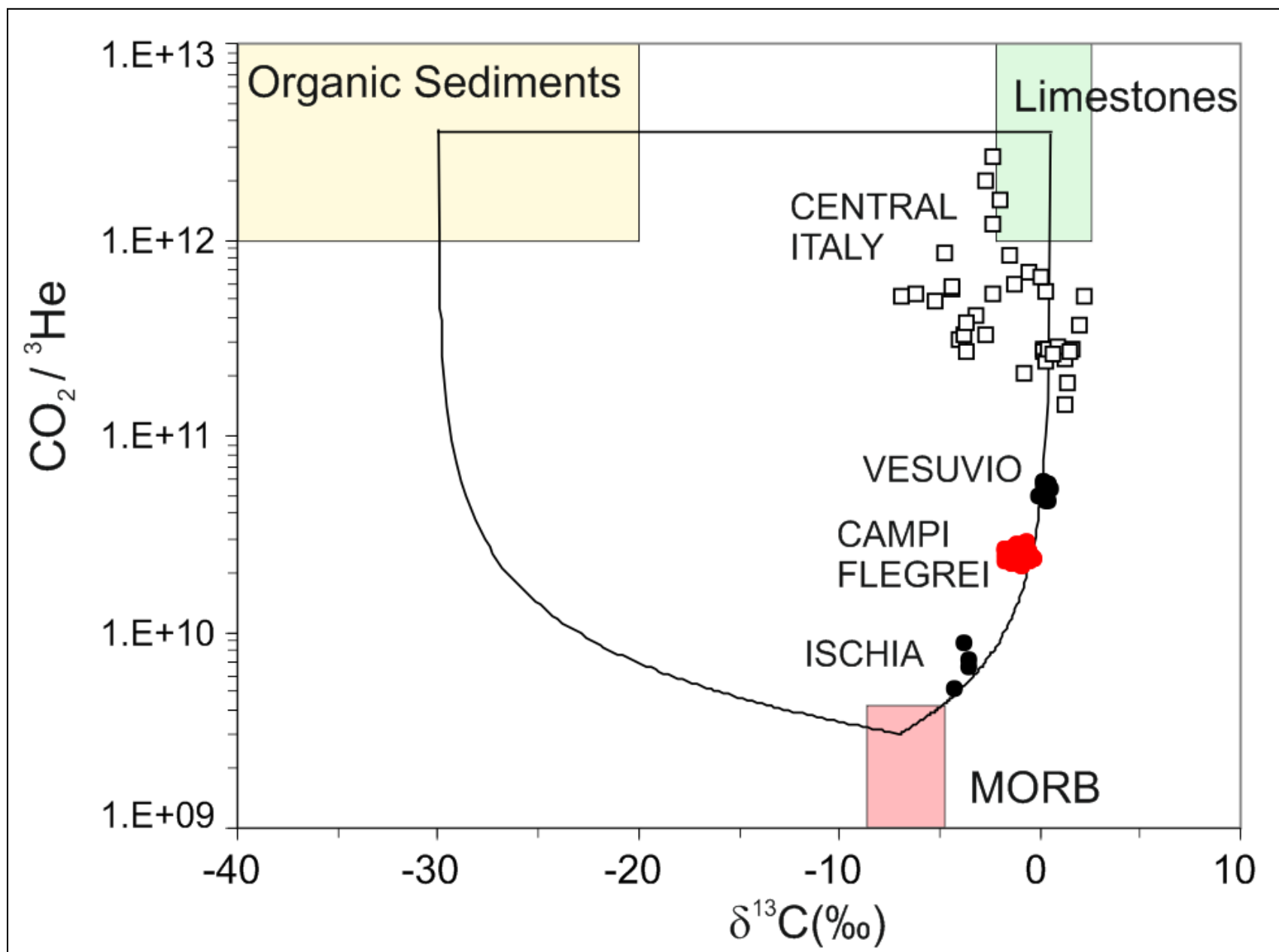
$$(\text{CO}_2/{}^3\text{He})_{\text{Lim}} = 1 \times 10^{13}$$

Different sources of CO_2 :
 Sediments (carbonates vs organic-rich sediments)
 Mantle degassing
 How can the CO_2 source be recognized?

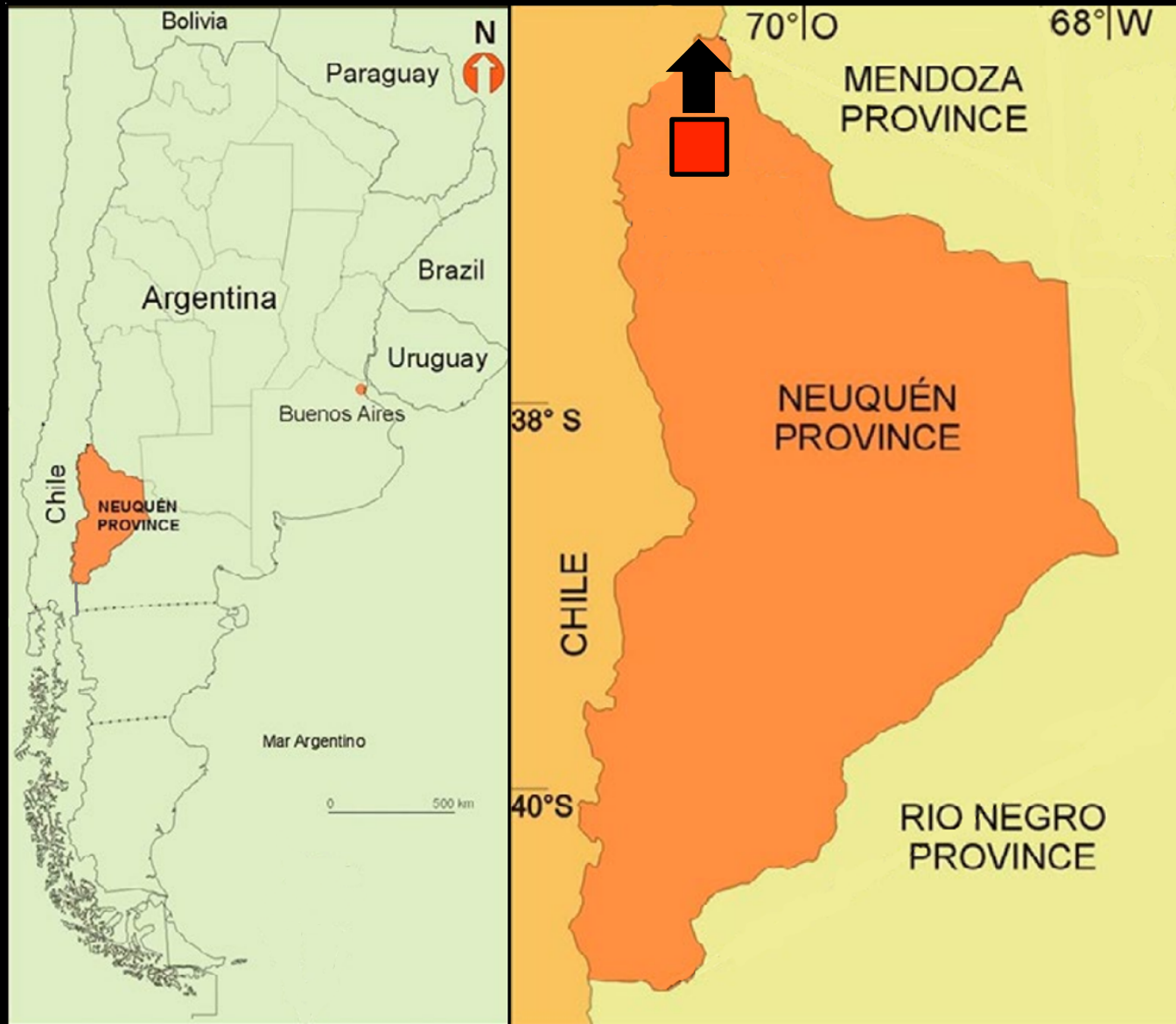


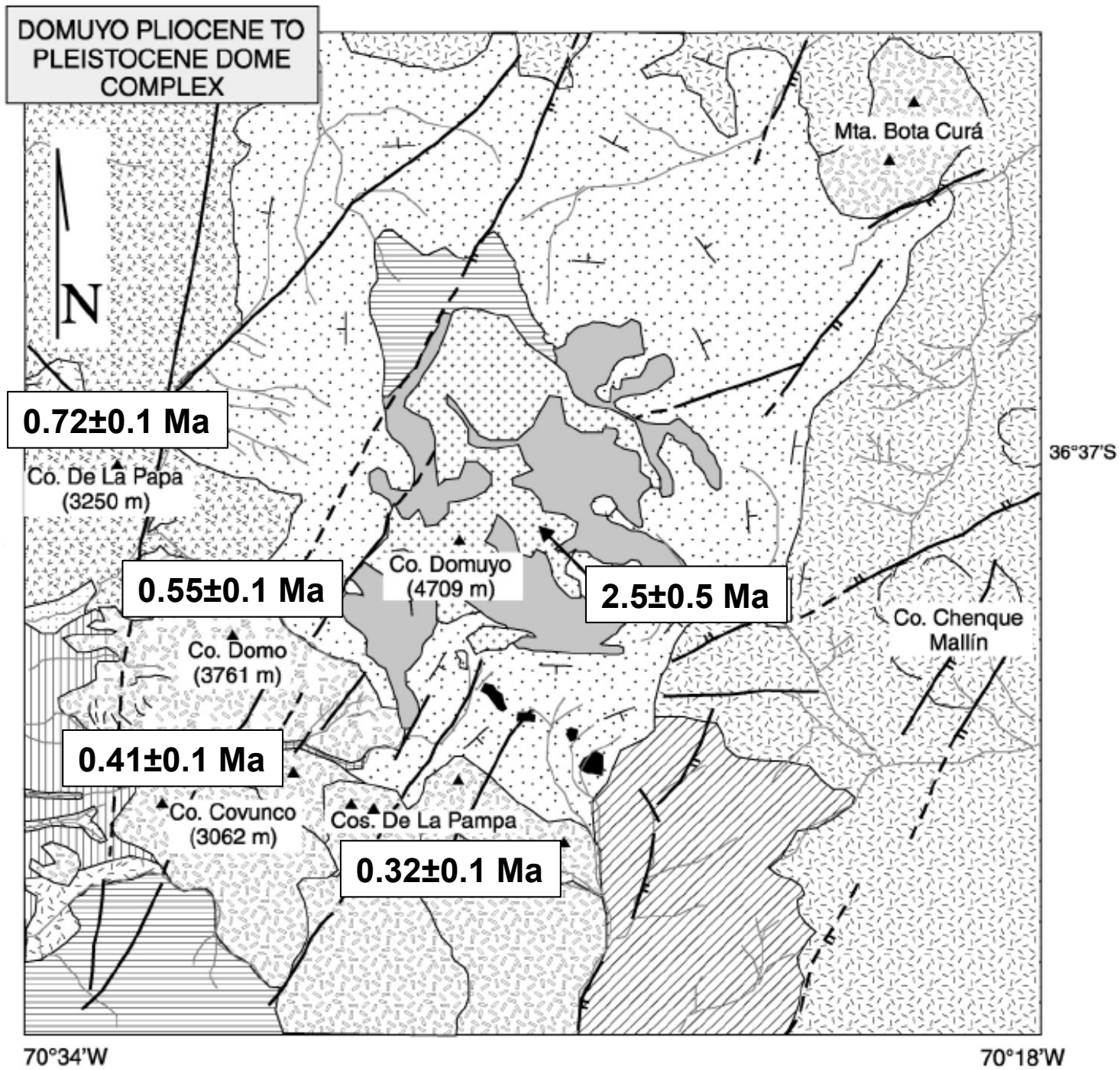
- Tacora (Chile)
- Lascar (Chile)
- Lastarria (Chile)
- ▨ Vulcano (Italy)
- Azacualpa geoth. Field (Honduras)



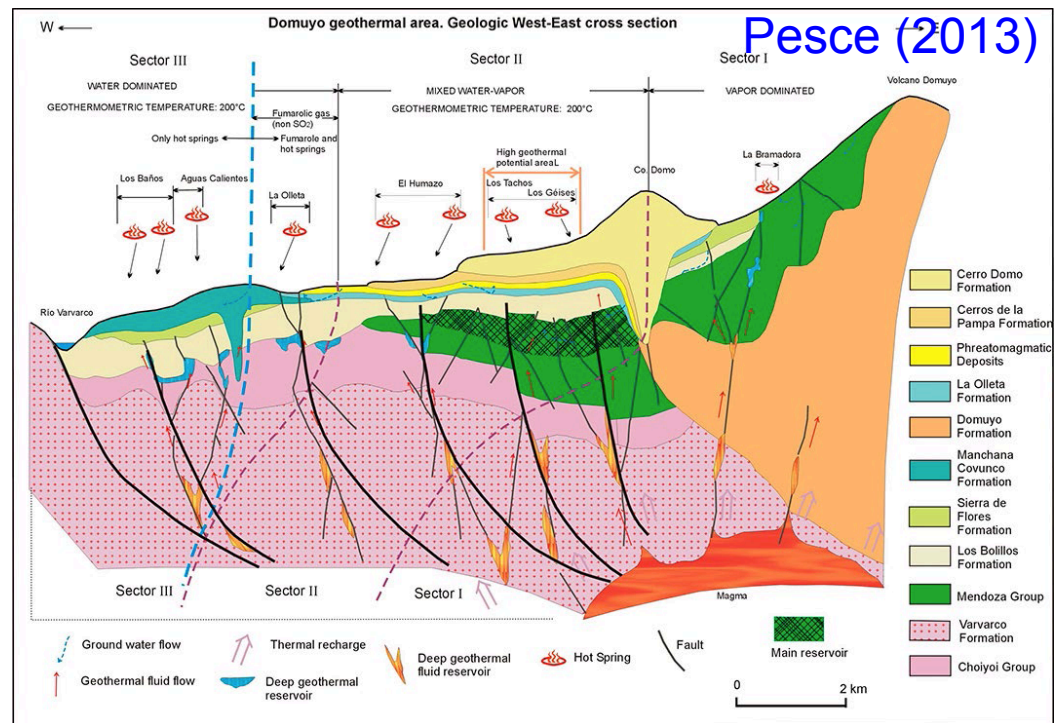
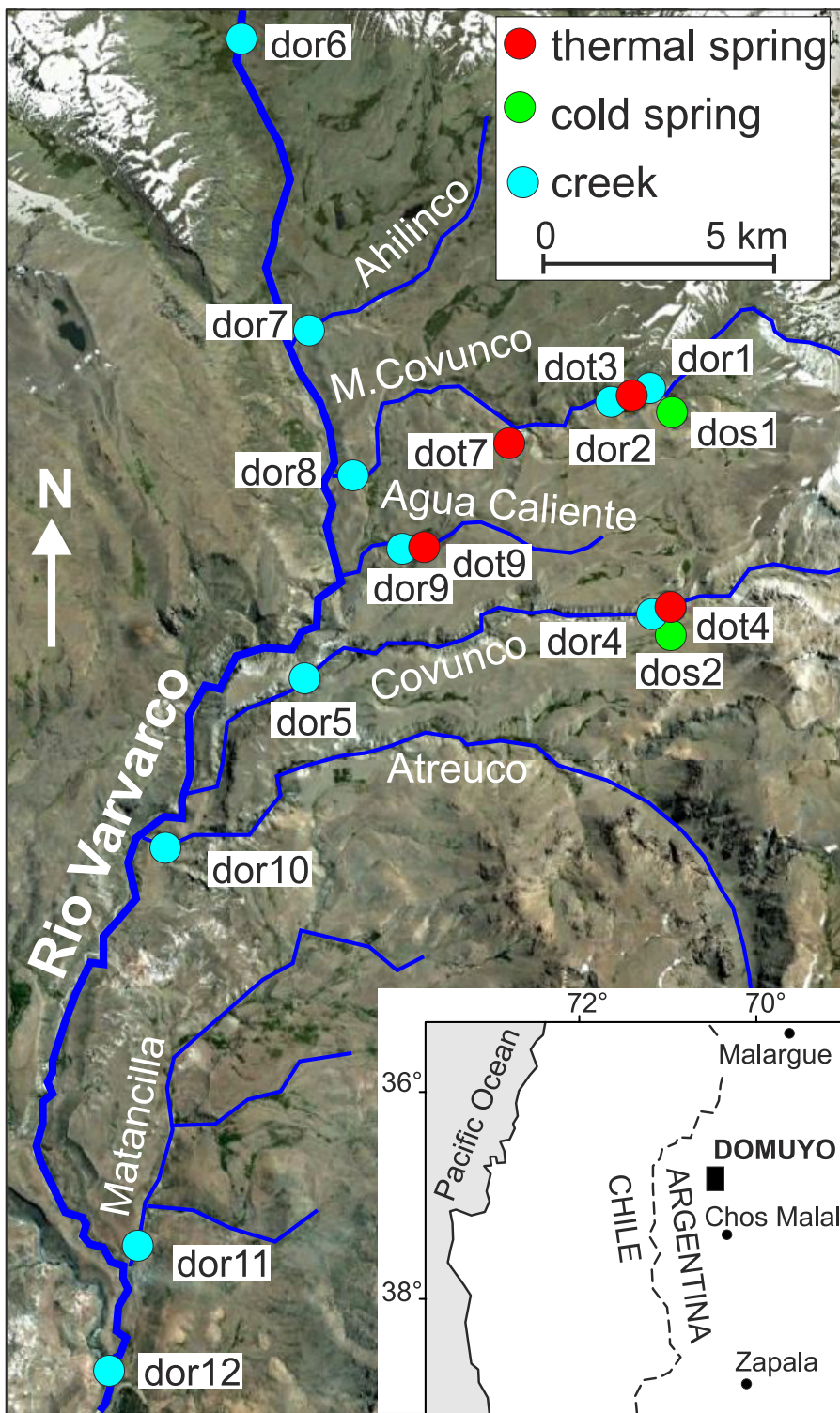


The Domuyo Volcanic Complex

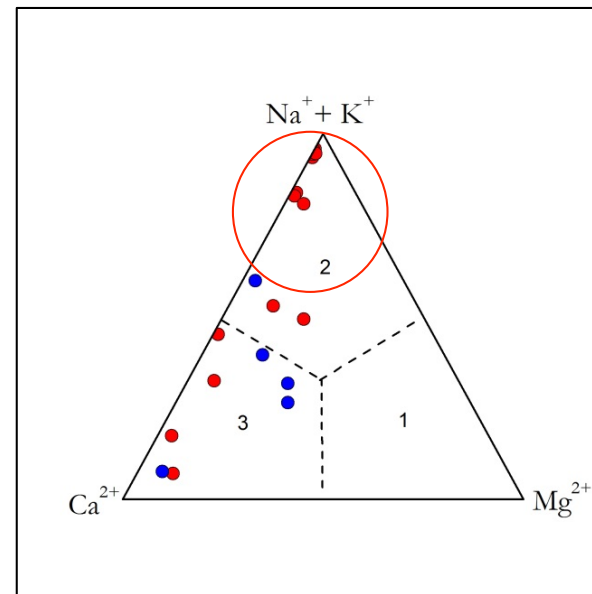
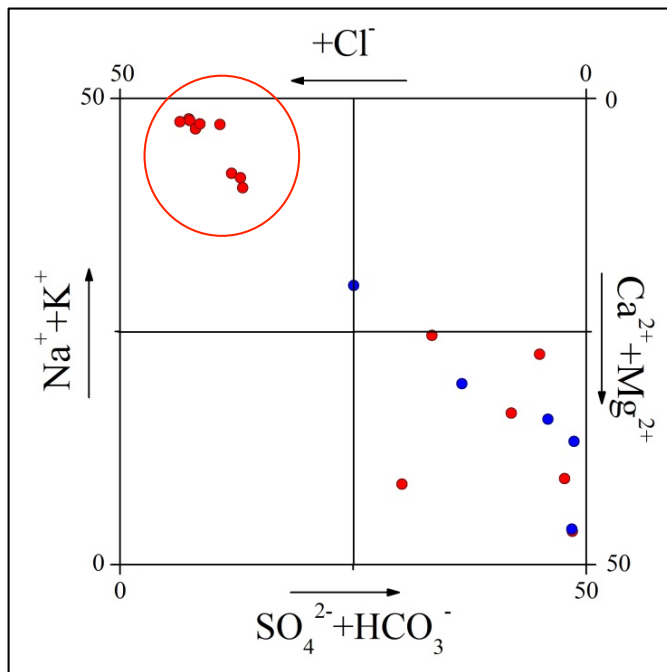
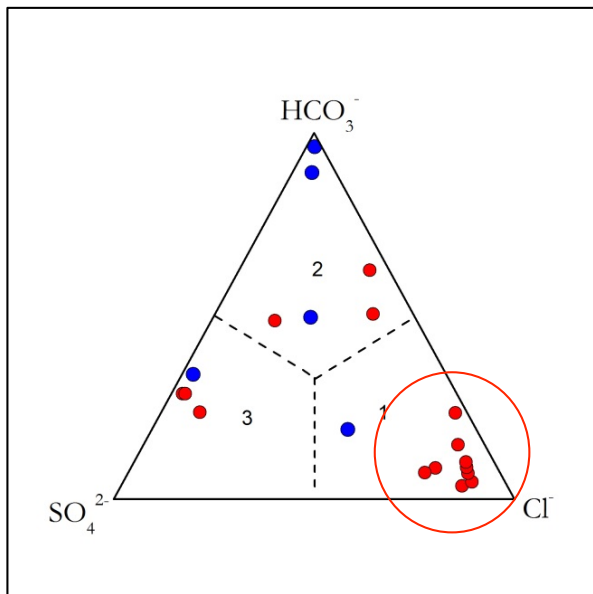


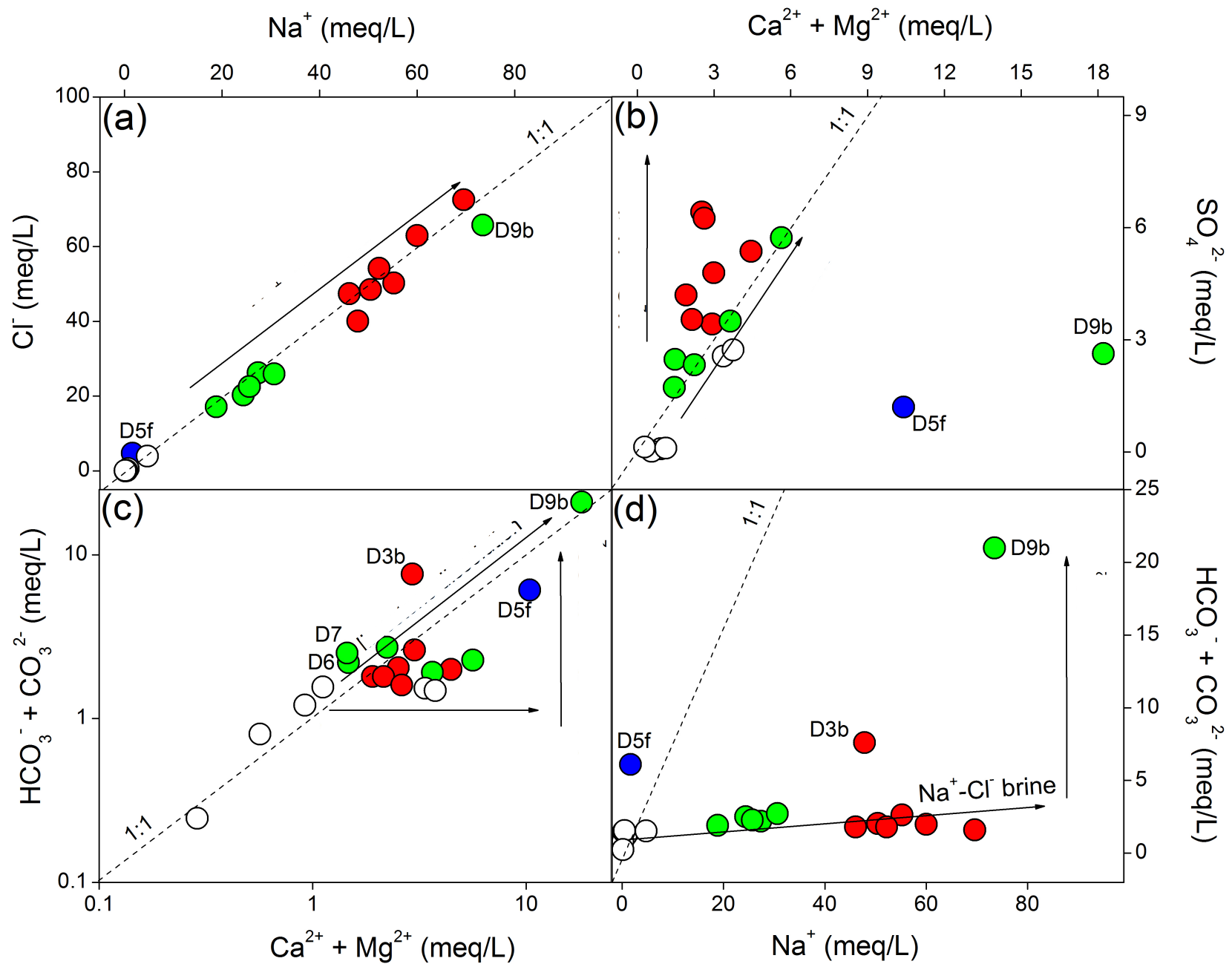




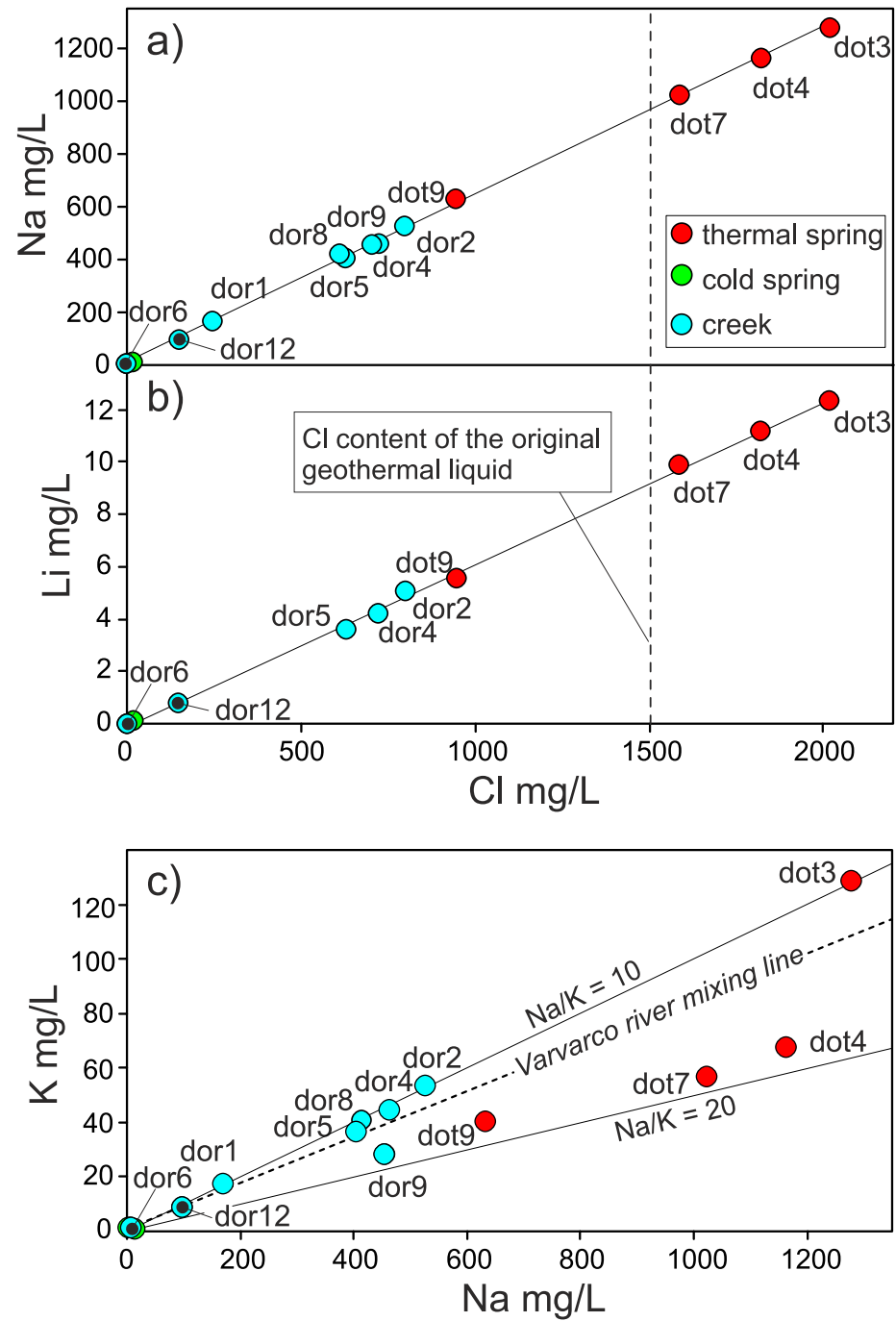


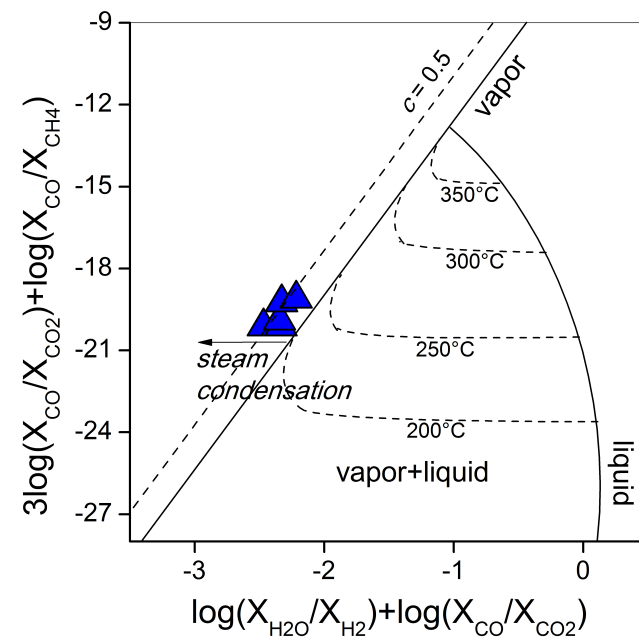
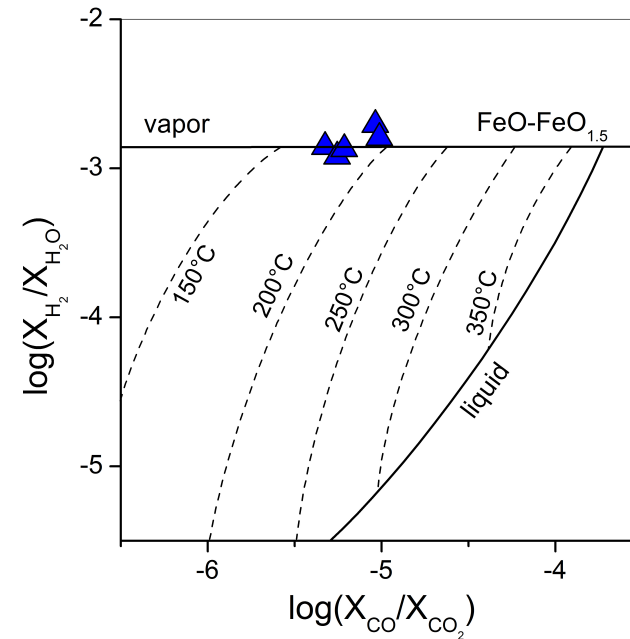
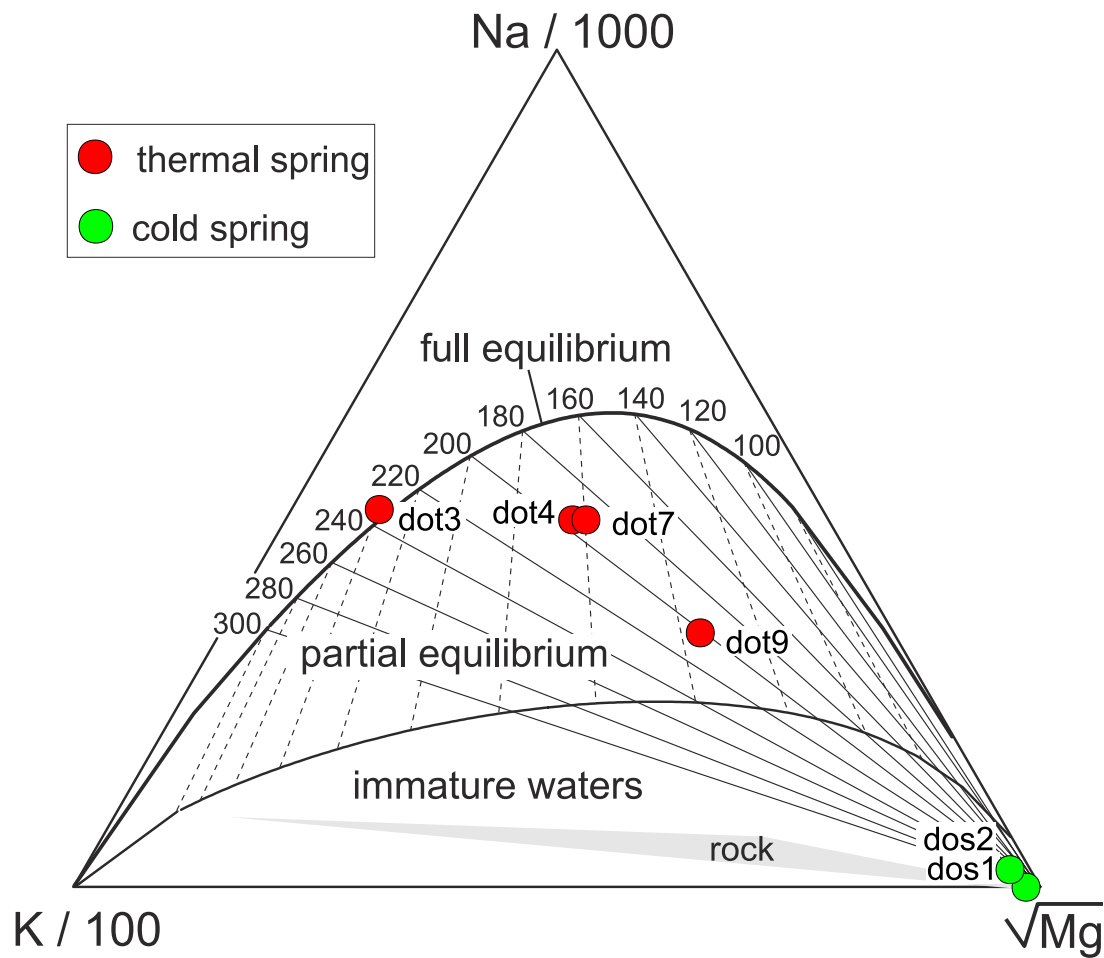
Acque

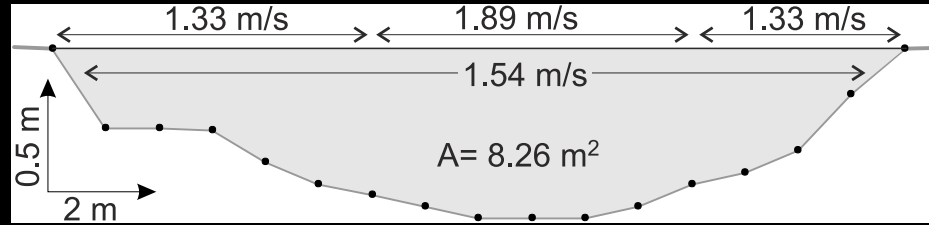




Iso-enthalpic boiling:
0.17 to 0.26







Between 11,000 and 15,700 kg s⁻¹ Cl: 1,880 g s⁻¹

Computation of the total thermal release

$$Q_H = Q_{Cl} / Cl_t \times H_t$$

Thermal energy release \rightarrow Q_H
 Cl flux in (kg/sec) the river \rightarrow Q_{Cl}
 Cl content in the original liquid \rightarrow Cl_t
 Enthalpy (J/g) at the 220 °C \rightarrow H_t

The equation was solved by a Monte Carlo procedure:
 1.1 ± 0.2 GW